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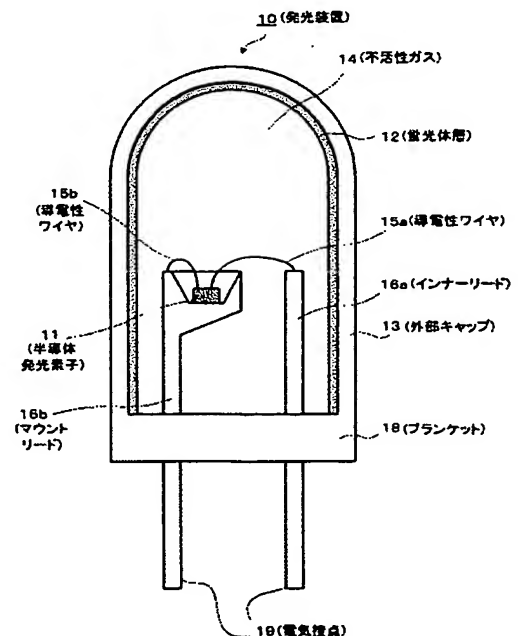
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(54) 【発明の名称】 発光装置及び照明装置

(57) 【要約】

【課題】 蛍光体の耐久性を向上させ、高輝度光を発生させることのできる発光装置、それを使用した照明装置を提供すること。

【解決手段】 ブランケット18と、ブランケット18の上部を覆い、例えばガラス等の光透過性材料でドーム型に形成された外部キャップ13と、ブランケット18に取り付けられたマウントリード16b及びインナーリード16aと、ブランケット18の下部に取り付けられ、マウントリード16b及びインナーリード16aと導通する電気接点19と、マウントリード16b上部のカップ内に収納された半導体発光素子11と、赤色蛍光体がバインダー樹脂中に混合分散され、外部キャップ13の内側に塗布された被膜の蛍光体層12と、インナーリード16aと半導体発光素子11とを導通する導電性ワイヤ15aと、半導体発光素子11とマウントリード16bとを導通する導電性ワイヤ15bと、を有し、外部キャップ13の内部は、真空又は窒素ガス、アルゴンガス等の不活性ガス14が充填されている発光装置10。



(2)

【特許請求の範囲】

【請求項1】

近紫外光から可視光領域迄の光を発光する発光素子と、
前記発光素子からの光により発光する少なくとも1種の蛍光性錯体を含有する蛍光体と、を備え、
前記蛍光体が、低酸素濃度雰囲気下に置かれていることを特徴とする発光装置。

【請求項2】

前記発光素子は、360nmから470nmの範囲にピーク波長を有する光を発光する半導体発光素子であることを特徴とする請求項1記載の発光装置。

【請求項3】

前記蛍光体が、光透過性材料により形成された容器内部に設置されていることを特徴とする請求項1又は2記載の発光装置。

【請求項4】

前記容器内部が、容器内面であることを特徴とする請求項3記載の発光装置。

【請求項5】

前記蛍光体は、酸素濃度が100ppm以下の雰囲気下に置かれていることを特徴とする請求項1乃至4いずれか1項記載の発光装置。

【請求項6】

前記蛍光体は、真空又は不活性ガスの雰囲気下に置かれていることを特徴とする請求項1乃至5いずれか1項記載の発光装置。

【請求項7】

前記蛍光性錯体が、希土類イオン錯体から選ばれることを特徴とする請求項1乃至6いずれか1項記載の発光装置。

【請求項8】

前記希土類イオン錯体が、芳香族環を含む置換基を有する β -ジケトン又は芳香族環を含む置換基を有するカルボン酸から誘導されるアニオンを配位子とする希土類イオン錯体から選ばれることを特徴とする請求項7記載の発光装置。

【請求項9】

前記希土類イオン錯体は、ルイス塩基を補助配位子とすることを特徴とする請求項7又は8記載の発光装置。

【請求項10】

前記希土類イオン錯体は、前記発光素子からの光により赤色に発光するユーロピウム錯体であることを特徴とする請求項7乃至9いずれか1項記載の発光装置。

【請求項11】

前記蛍光体は、前記蛍光性錯体を溶解又は分散させて混合した樹脂組成物であることを特徴とする請求項1乃至10いずれか1項記載の発光装置。

【請求項12】

前記発光素子からの光により発光する青色蛍光体及び緑色蛍光体をさらに備えることを特徴とする請求項1乃至11いずれか1項記載の発光装置。

【請求項13】

発光素子が容器の内部に設けられ、前記発光素子と蛍光体とが空間を隔て又は他の層を介して前記容器の内部に設けられていることを特徴とする請求項3乃至12いずれか1項記載の発光装置。

【請求項14】

前記蛍光体は、前記発光素子と光拡散層を介して前記容器の内部に設けられていることを特徴とする請求項3乃至13いずれか1項記載の発光装置。

【請求項15】

前記蛍光体は、無機蛍光体からなる層と前記蛍光性錯体を含む蛍光体からなる層との積層体であることを特徴とする請求項1乃至14記載の発光装置。

【請求項16】

(3)

請求項1乃至15いずれか1項記載の発光装置を備えることを特徴とする照明装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は発光装置及び照明装置に関し、より詳しくは、蛍光体の耐久性が改良された発光装置、これを使用した照明装置に関する。

【0002】

【従来の技術】

従来、放電ランプや半導体発光素子の光を蛍光体で色変換させた発光装置が照明等に使用されている。これらの発光装置は、青、赤及び緑色光を混合し、白色その他の様々な色の光を、広い色再現範囲で、むらなくかつ演色性良く発光させるために多くの検討がなされている。なかでも、発光ダイオード(LED)や半導体レーザー(LD)等の半導体発光素子を用いた発光装置は、発光効率が高く、水銀を使用しない等の環境対策面の利点もあり、LEDやLDと蛍光体を組み合わせた発光装置の開発が盛んに行われている。

【0003】

特に、LEDやLDと、 β -ジケトンのアニオンを配位子とするユーロピウム(Eu)錯体を含有する有機赤色蛍光体とを組み合わせ使用する発光装置は、 $Y_2O_3:Eu$ 等の無機赤色蛍光体を使用する蛍光灯と比べて、近紫外光から可視光の光を効率よく吸収し、高輝度な発光を得ることができる装置として報告されている(例えば、特許文献1及び特許文献2参照)。

【0004】

【特許文献1】

特開平10-12925号公報

【特許文献2】

特表2000-509912号公報

【0005】

【発明が解決しようとする課題】

ところで、このような有機赤色蛍光体等に用いられる希土類イオン錯体等の蛍光性錯体は光劣化し易いことが知られており、また、近年、LEDやLDの開発は、より短波長の光を発光する方向に向けられている。その結果、エネルギー的に大きい光が照射された蛍光体や封止材等の劣化が著しくなり、このため、耐久性が要求される発光装置の実用化の必要性が生じている。

【0006】

本発明は、このような蛍光性錯体を使用する発光装置を開発する際に浮き彫りになった問題を解決すべくなされたものである。即ち、本発明の目的は、発光特性に優れるユーロピウム錯体をはじめとする希土類イオン錯体等の蛍光性錯体を含有する蛍光体の耐久性を大幅に向上させ、高強度の発光を発生させることのできる発光装置、これを使用した照明装置を提供することを目的とするものである。

【0007】

【課題を解決するための手段】

本発明者等は、耐久性が高い発光装置を提供すべく、種々の条件下でユーロピウム錯体等の蛍光性錯体の光劣化について検討を行ったところ、光劣化に酸素が関与することが明らかとなり、酸素濃度を下げた減圧下又は窒素ガス、アルゴン等の不活性ガス中で、蛍光性錯体の耐光性が向上することを見出した。即ち、本発明が適用される発光装置は、近紫外光から可視光領域迄の光を発光する発光素子と、この発光素子からの光により発光する少なくとも1種の蛍光性錯体を含有する蛍光体と、を備え、蛍光体が、低酸素濃度雰囲気下に置かれていることを特徴とするものである。

【0008】

本発明が適用される発光装置に使用する発光素子として、360nmから470nmの範囲にピーク波長を有する光を発光する半導体発光素子を用い、この発光素子と蛍光性錯体

(4)

とを組み合わせることにより、無機赤色蛍光体を使用する発光装置と比べて、高輝度な発光を得ることができる。また、蛍光性錯体を含有する蛍光体は、光透過性材料により形成された容器内部に設置することを特徴とすれば、近紫外光から可視光の光を効率よく吸収することができる。

【0009】

さらに、本発明が適用される発光装置に使用する蛍光体は、酸素濃度が100ppm以下の雰囲気下に置かれていることを特徴とすれば、蛍光体に含まれる蛍光性錯体の耐光性が顕著に向上する。また、蛍光体が置かれる酸素濃度が100ppm以下の雰囲気下とするには、真空又は不活性ガスの雰囲気下であることが好ましい。

【0010】

また、本発明が適用される発光装置に使用する蛍光体に含まれる蛍光性錯体は、希土類イオン錯体から選ばれることが好ましい。特に、本発明が適用される発光装置に使用する蛍光体は、芳香族環を含む置換基を有するβ-ジケトン又は芳香族環を含む置換基を有するカルボン酸から誘導されるアニオンを配位子とする希土類イオン錯体から選ばれる蛍光性錯体を含有することを特徴とすることが好ましい。また、希土類イオン錯体は、ルイス塩基を補助配位子とすることが、輝度向上の点から好ましい。中でも、希土類イオン錯体は、ユーロピウム錯体であることが好ましい。

【0011】

この蛍光体の態様としては、蛍光性錯体を溶解又は分散させて混合した樹脂組成物であることが好ましい。また、本発明が適用される発光装置は、ユーロピウム錯体等の発光素子からの光により赤色に発光する蛍光体と共に、発光素子からの光により発光する青色蛍光体及び緑色蛍光体をさらに備えることを特徴とすれば、白色発光装置とすることができる。

【0012】

一方、本発明が適用される発光装置は、光透過性材料により形成され、内部が低酸素濃度雰囲気に保たれた容器と、この容器の内部に設けられ、近紫外光から可視光領域迄の光を発光する発光素子と、発光素子と空間を隔て又は他の層を介して容器の内部に設けられた蛍光体と、を備えることを特徴とすれば、耐久性に優れ、高強度の発光を発生させることのできる一体型の発光装置として把握することができる。

【0013】

この場合、蛍光体は、発光素子と光拡散層を介して低酸素濃度雰囲気に保たれた容器の内部に設けられていることが好ましい。また、蛍光体は、無機蛍光体と共に使用する場合には、無機蛍光体と蛍光性錯体を含有する蛍光体とを混合してもよい。さらに、蛍光体が半導体発光素子に近接して配置される場合は、無機蛍光体からなる層と蛍光性錯体を含む蛍光体からなる層とがそれぞれ分離された積層体であることが好ましい。

【0014】

そして、本発明が適用される発光装置を備える照明装置を提供することができる。

【0015】

【発明の実施の形態】

本実施の形態が適用される発光装置は、近紫外光から可視光領域迄の光を発光する発光素子と、この発光素子からの光により発光する少なくとも1種の蛍光性錯体を含有する蛍光体と、を備え、蛍光体が、低酸素濃度雰囲気下に置かれている。ここで低酸素濃度雰囲気下とは、空気より酸素濃度が低い雰囲気下のことであり、そのような雰囲気下に蛍光体を置くことにより、蛍光性錯体の耐久性が向上する。減圧又は真空にすることにより、あるいは不活性ガスの雰囲気下とすることにより、低酸素濃度雰囲気下になるが、蛍光性錯体の耐光性をより向上させるためには、酸素濃度が1000ppm以下であることが好ましい。

次に、本実施の形態が適用される発光装置について説明する。図1は、本実施の形態における発光装置を説明するための図である。図1に示された発光装置10は、ブランケット18と、ブランケット18の上部を覆い、例えばガラス等の光透過性材料でドーム型に形

(5)

成された外部キャップ13と、ブラケット18に取り付けられたマウントリード16b及びインナーリード16aと、ブラケット18の下部に取り付けられ、マウントリード16b及びインナーリード16aと導通する電気接点19と、マウントリード16b上部のカップ内に収納された半導体発光素子11と、マウントリード16b上部のカップ内に充填され、赤色蛍光体がバインダー樹脂中に混合分散され、外部キャップ13の内側に塗布された被膜の蛍光体層12と、インナーリード16aと半導体発光素子11とを導通する導電性ワイヤ15aと、半導体発光素子11とマウントリード16bとを導通する導電性ワイヤ15bと、を有し、外部キャップ13の内部は、真空又は窒素ガス、アルゴンガス等の不活性ガス14が充填されている。

【0016】

半導体発光素子11は、近紫外光から可視光領域迄の光を発光し、この光を蛍光体層12に含まれる蛍光体が吸収し、より長波長の可視光を発光する。外部キャップ13の内部に窒素ガスを充填する代わりに、真空状態に保つことにより、蛍光体層12の耐光性を向上させ、発光装置10の耐久性を高めることも可能である。外部キャップ13の内部における酸素濃度と蛍光性錯体を含有する蛍光体層12に含まれる蛍光性錯体の劣化挙動との関係は明確ではないが、蛍光性錯体を、酸素濃度100ppm以下、好ましくは20ppm以下の雰囲気下において、半導体発光素子11から光を照射すると、耐光性は著しく向上する。また、低温度下においても耐光性は向上する。

【0017】

半導体発光素子11としては、発光スペクトルのピーク波長が360nmから470nmの範囲にあるレーザダイオード(LD)又は発光ダイオード(LED)が用いられる。このようなレーザダイオード(LD)又は発光ダイオード(LED)としては、特に限定されないが、例えば、380nmから470nmにピーク波長を有するLD、LEDが好ましい。ピーク波長が過度に短波長側にある半導体発光素子は、錯体及び樹脂等の有機化合物が光劣化しやすい傾向があるので好ましくない。又、ピーク波長が過度に長波長側にある場合は、ユーロピウム錯体の配位子の三重項エネルギーレベルが低くなり、発光可能な配位子の選択の幅が狭くなるので好ましくない。

【0018】

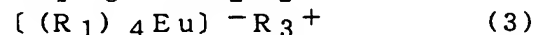
蛍光体層12は、蛍光性錯体と樹脂からなる樹脂組成物を、外部キャップ13の内側に塗布により形成された被膜の形態で設けられている。蛍光性錯体としては、特に限定されないが、通常、1種または2種以上の配位子アニオンと3価の希土類元素のイオンとの錯体である希土類イオン錯体を使用される。希土類元素としては、Sm、Eu、Tb、Er、Tm等が挙げられる。なかでも、赤色蛍光体としてはEu(ユーロピウム)元素、青色蛍光体としてはTm(ツリウム)元素、緑色蛍光体としてはTb(テルビウム)元素のイオン錯体が好んで用いられる。尚、蛍光体層12には、希土類イオン錯体の他、その他の有機蛍光体、無機蛍光体を適宜併用することも可能である。

【0019】

希土類イオン錯体の中でも、特に、無機蛍光体では困難である近紫外光照射において高輝度に発光する赤色蛍光体として、ユーロピウム錯体が好ましい。また、希土類イオン錯体は、芳香族環を含む置換基を有するβ-ジケトンアニオン、あるいは芳香族基を含む置換基を有するカルボン酸イオンを配位子とする錯体であることが好ましい。以下、希土類イオン錯体としてユーロピウム錯体を例に挙げて説明するが、これに限られるものではない。

【0020】

芳香族環を含む置換基を有するβ-ジケトンアニオンを配位子とする錯体としては、例えば、下記一般式(1)、(2)及び(3)のいずれか1つの式で表されるユーロピウム錯体が挙げられる。



(6)

(式(1)、(2)及び(3)中、 R_1 は芳香族環を含む置換基を有する β -ジケトンのアニオンであり、 R_2 はルイス塩基からなる補助配位子であり、 R_3^+ は4級アンモニウムイオンである。)

【0021】

式(1)、(2)及び(3)における芳香族環を含む置換基を有する β -ジケトンとしては、芳香族環を含む置換基と β -ジケトンとをその構造中に含めば、その連結方法は、直接でも2価の基で連結してもよいが、少なくとも一方のケトンに直接芳香族環が連結しているものが好ましく、少なくとも1つの芳香族基を有することが好ましく、さらに、この芳香族基としては、置換基を有することがある芳香族炭化水素化合物又は芳香族複素環化合物が挙げられる。芳香族炭化水素化合物としては、例えば、ベンゼン、ナフタリン、フェナントレン、フルオレン等が挙げられる。芳香族複素環化合物としては、フラン、チオフェン、ピラゾリン、ピリジン、ベンゾチオフェン、カルバゾール、ジベンゾフラン、ジベンゾチオフェン等の酸素、窒素、硫黄原子を含む複素環化合物が挙げられる。

【0022】

また、これらの芳香族炭化水素化合物又は芳香族複素環化合物の置換基としては、例えば、メチル、エチル、プロピル、ブチル等のアルキル基；トリフルオロメチル、ペンタフルオロエチル等のフルオロアルキル基；メトキシ、エトキシ等のアルコキシ基；フェニル、ナフチル基等のアリール基；ベンジル、フェネチル等のアリールオキシ基；ヒドロキシ基；アリル基；アセチル、プロピオニル等のアシル基；アセトキシ、プロピオニルオキシ、ベンゾイルオキシ等のアシルオキシ基；メトキシカルボニル、エトキシカルボニル等のアルコキシカルボニル基；フェノキシカルボニル等のアリールオキシカルボニル基；カルボキシ基；カルバモイル基；アミノ基；ジメチルアミノ、ジエチルアミノ、メチルベンジルアミノ、ジフェニルアミノ、アセチルメチルアミノ等の置換アミノ基；メチルチオ、エチルチオ、フェニルチオ、ベンジルチオ等の置換チオ基；メルカプト基；エチルスルフォニル、フェニルスルフォニル等の置換スルフォニル基；シアノ基；フルオロ、クロロ、ブロモ、ヨード等のハロゲン基等が挙げられる。これらの置換基は、互いに結合して環を形成してもよい。

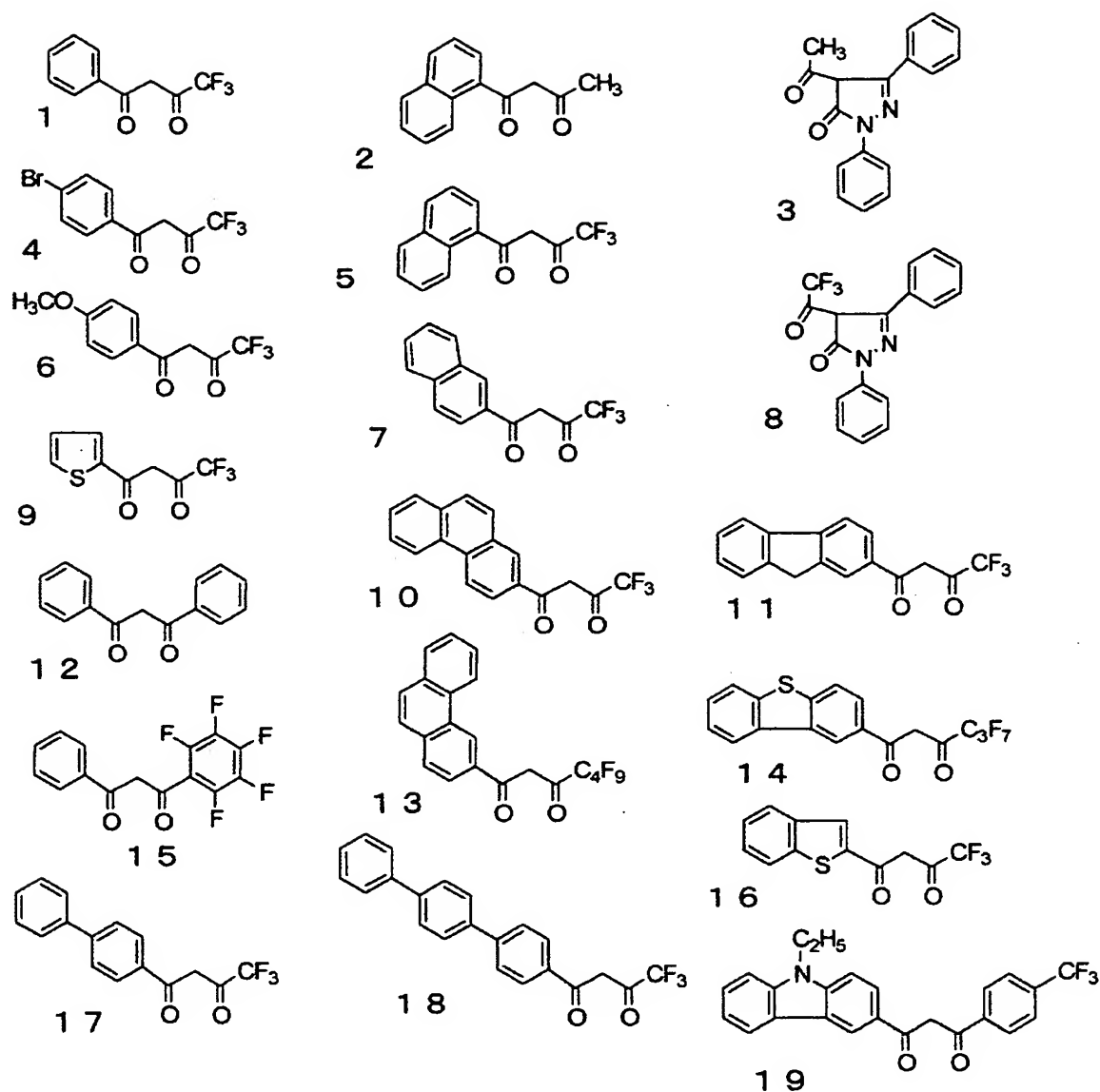
【0023】

β -ジケトンとを構成する芳香族基以外の置換基としては、前述した芳香族炭化水素化合物又は芳香族複素環化合物の置換基と同様な置換基（但し、ハロゲン基は除く）が挙げられる。芳香族環を含む置換基を有する β -ジケトンの具体例(1~19)を以下に示す。なお、本実施の形態においてはこれらに限定されるものではない。

【0024】

【化1】

(7)



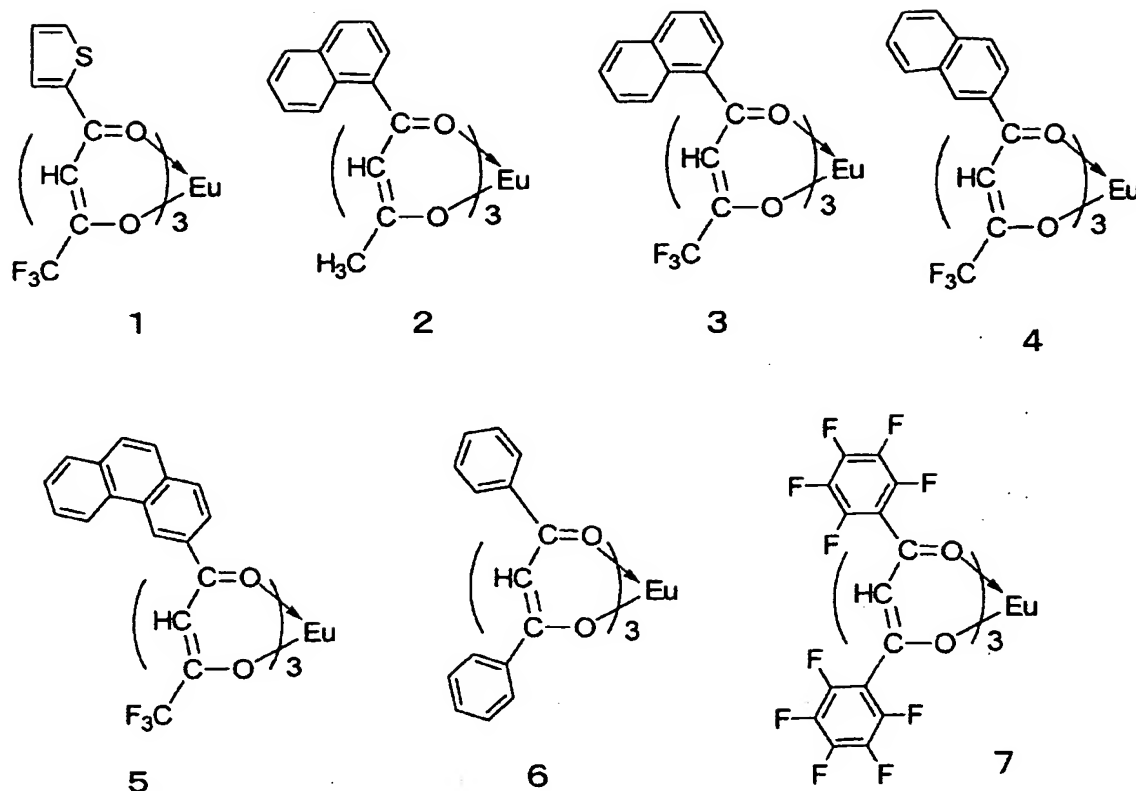
【0025】

一般式(1)で表されるユーロピウム錯体の具体例(1~7)を以下に示す。なお、本実施の形態においてはこれらに限定されるものではない。

【0026】

【化2】

(8)



【0027】

次に、一般式(2)で表されるユーロピウム錯体について説明する。一般式(2)におけるルイス塩基からなる補助配位子(R_2)としては特に限定されないが、通常、ユーロピウムイオンに配位可能な窒素原子又は酸素原子を有するルイス塩基化合物から選択される。それらの例としては、置換基を有することがあるアミン、アミノキシド、ホスフィンオキシド、スルホキシド等が挙げられる。補助配位子として使用される2個のルイス塩基化合物は、それぞれ異なる化合物でもよく、又、2個の化合物で1つの化合物を形成していてもよい。

【0028】

具体的には、例えば、アミンとしては、ピリジン、ピラジン、キノリン、イソキノリン、フェナントリジン、2,2'-ビピリジン、1,10-フェナントロリン等が挙げられる。アミノキシドとしては、ピリジン-N-オキシド、2,2'-ビピリジン-N,N'-ジオキシド等の上記アミンのN-オキシドが挙げられる。ホスフィンオキシドとしては、トリフェニルホスフィンオキシド、トリメチルホスフィンオキシド、トリオクチルホスフィンオキシド等が挙げられる。スルホキシドとしては、ジフェニルスルホキシド、ジオクチルスルホキシド等が挙げられる。これらに置換する置換基としては、前述した置換基が例示される。中でも、特に、アルキル基、アリール基、アルコシキル基、アラルキル基、アリーールオキシ基、ハロゲン基等が好ましい。

【0029】

これらのルイス塩基化合物の中でも、ビピリジンやフェナントロリン等のように、分子内に配位する原子、例えば窒素原子等の2個存在する場合は、1つのルイス塩基化合物で2個の補助配位子と同様な働きをさせてもよい。なお、これらのルイス塩基化合物に置換する置換基としては、前述した置換基が例示される。中でも、特に、アルキル基、アリール基、アルコシキル基、アラルキル基、アリーールオキシ基、ハロゲン基等が好ましい。

【0030】

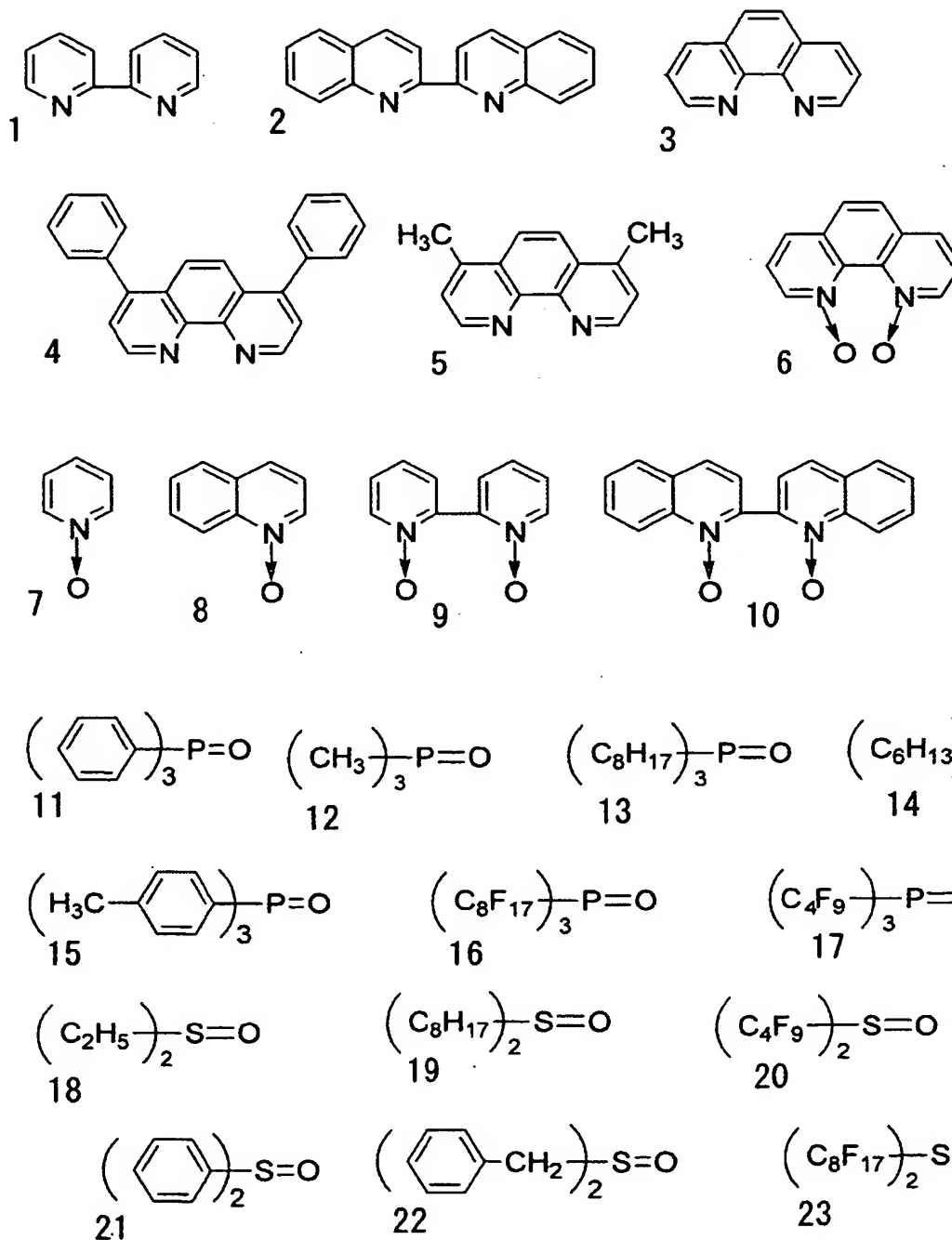
補助配位子として使用するルイス塩基化合物(R_2)の具体例(1~23)を以下に例示

(9)

する。なお、本実施の形態において使用するルイス塩基化合物は、これらに限定されるものではない。

【0031】

【化3】



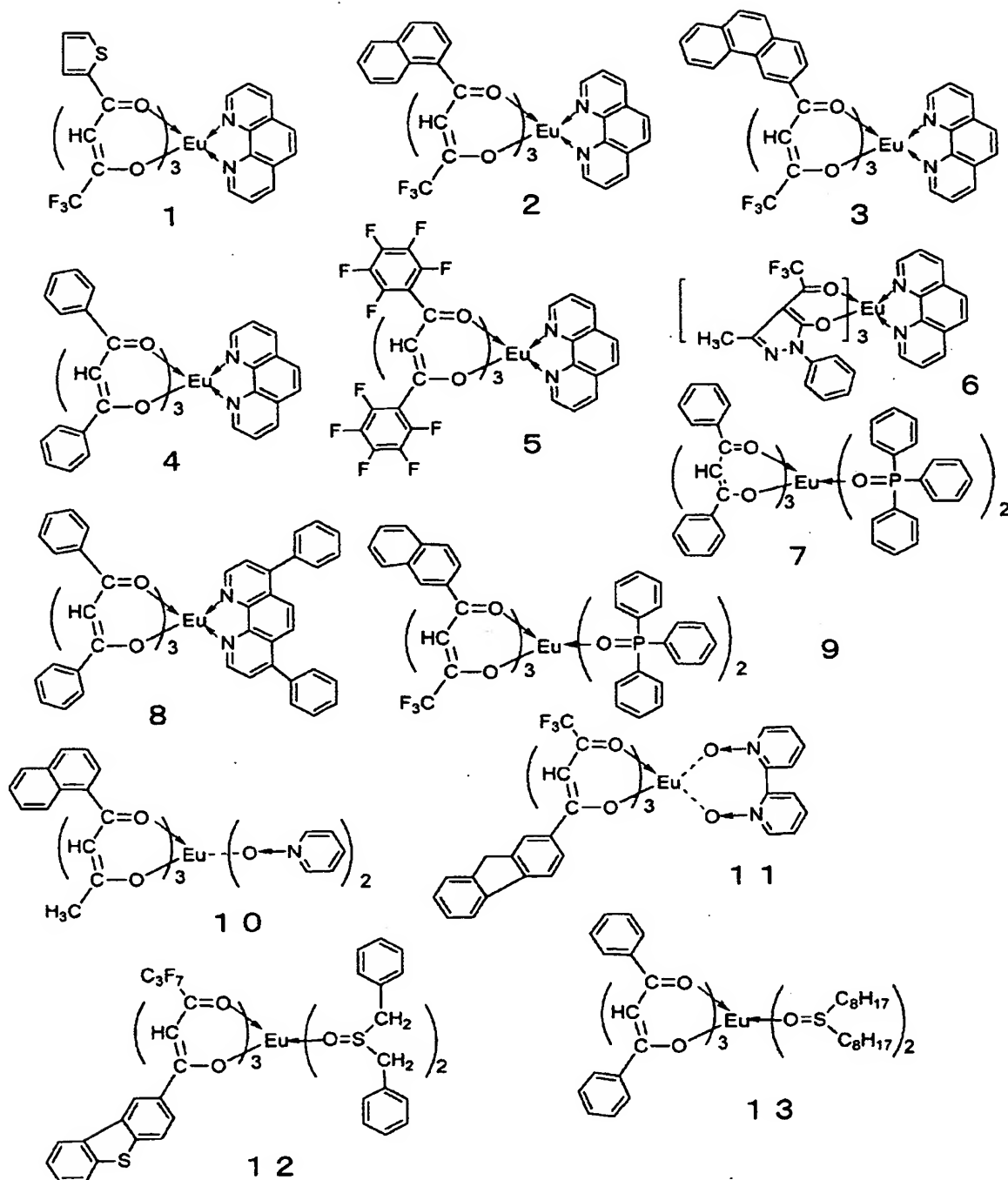
【0032】

一般式(2)で表されるユーロピウム錯体の具体例(1~13)を以下に示す。なお、本実施の形態においてはこれらに限定されるものではない。

【0033】

【化4】

(10)



【0034】

次に、一般式(3)で表されるユーロピウム錯体について説明する。一般式(3)におけるアンモニウムイオンとしては、アルキルアミン、アリールアミン、アラルキルイオンから誘導される4級アンモニウム塩が挙げられる。アミンの置換基としては、メチル、エチル、プロピル、ブチル、ヘキシル、オクチル等のアルキル基；ヒドロキシエチル、メトキシエチル等の置換アルキル基；フェニル、トリル等のアリール基；ベンジル、フェネチル基等のアリールアルキル基等が挙げられる。

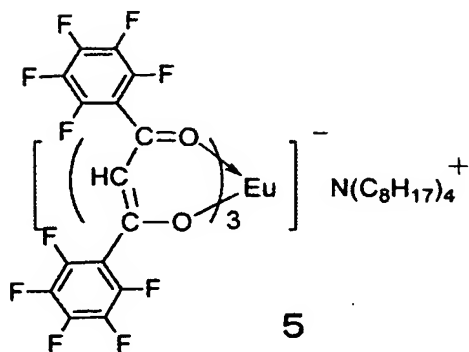
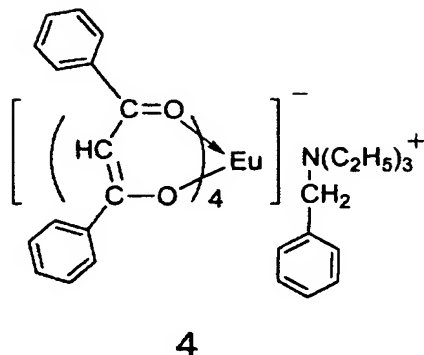
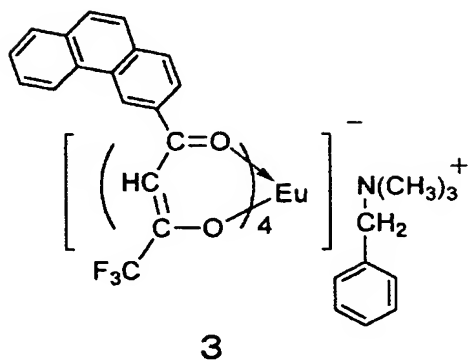
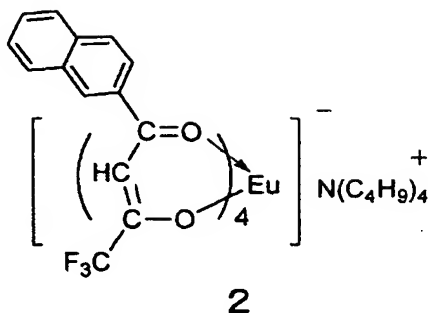
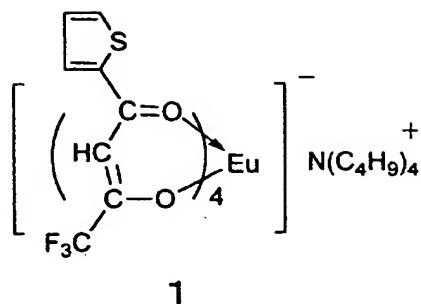
【0035】

一般式(3)で表されるユーロピウム錯体の具体例(1～5)を以下に示す。なお、本実施の形態においてはこれらに限定されるものではない。

【0036】

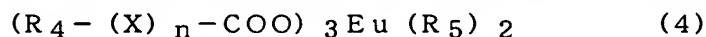
【化5】

(11)



【0037】

希土類イオン錯体のもう一つの化合物である、芳香族基を含む置換基を有するカルボン酸イオンを配位子とする錯体としては、例えば、下記一般式(4)で表されるユーロピウム錯体が挙げられる。



(式中、 R_4 は、置換基を有することがある芳香族炭化水素環又は芳香族複素環を少なくとも1つ含む基であり、 X は、2価の連結基であり、 n は、0又は1であり、 R_5 は、ルイス塩基からなる補助配位子である。)

【0038】

一般式(4)で表される配位子は、芳香族環を少なくとも1つ含み、 π 電子を8個以上有し、 π 電子共役系を構成するカルボン酸イオンを配位子として用いることが、吸収波長域の点から好ましい。又、芳香族環の個数は、カルボン酸イオンの母体化合物の三重項エネルギーが、ユーロピウムイオン励起状態エネルギーレベルよりも高いものであれば特に制限されないが、通常、3環式以下の芳香族又は芳香族複素環を用いることが好ましい。芳香族環の個数が4環以上の場合、例えば、芳香族環を4環以上有するピレン等の化合物は、半導体発光素子11からの光を吸収して励起された三重項エネルギーが低くなり、ユ

(12)

ーロビウム錯体が発光しなくなるおそれがある。

【0039】

一般式(4)中の R_4 は、置換基を有することがある3環式以下の芳香族環、又は複素芳香族環から誘導される1価の基であることが好ましい。芳香族環としては、例えば、ベンゼン、ナフタリン、インデン、ビフェニレン、アセナフテン、フルオレン、フェナントレン、テトラリン、インダン、インデン等の芳香族単環式炭化水素又は芳香族縮合多環式炭化水素；ベンゾキノン、ナフトキノン、アントラキノン等の芳香族炭化水素から誘導される化合物等が挙げられる。複素芳香族環としては、フラン、ピロール、チオフェン、オキサゾール、イソキサゾール、チアゾール、イミダゾール、ピリジン、ベンゾフラン、ベンゾチオフェン、クマリン、ベンゾピラン、カルバゾール、キサントゲン、キノリン、トリアジン等の芳香族単環式複素環又は芳香族縮合多環式複素環等が挙げられる。

【0040】

また、 R_4 が有することがある置換基としては、メチル、エチル、プロピル、ブチル等のアルキル基；トリフルオロメチル、ペンタフルオロエチル等のフルオロアルキル基；シクロヘキシル基等のシクロアルキル基；エチニル基；フェニルエチニル、ピリジルエチニル、チエニルエチニル等のアリールエチニル基；メトキシ、エトキシ等のアルコキシ基；フェニル、ナフチル等のアリール基；ベンジル、フェネチル等のアラルキル基；フェノキシ、ナフトキシ、ビフェニルオキシ等のアリールオキシ基；ヒドロキシ基；アリル基；アセチル、プロピオニル、ベンゾイル、トルオイル、ビフェニルカルボニル等のアシル基；アセトキシ、プロピオニルオキシ、ベンゾイルオキシ等のアシルオキシ基；メトキシカルボニル、エトキシカルボニル等のアルコキシカルボニル基；フェノキシカルボニル等のアリールオキシカルボニル基；カルボキシ基；カルバモイル基；アミノ基；ジメチルアミノ、ジエチルアミノ、メチルベンジルアミノ、ジフェニルアミノ、アセチルメチルアミノ等の置換アミノ基；メチルチオ、エチルチオ、フェニルチオ、ベンジルチオ等の置換チオ基；メルカプト基；エチルスルフォニル、フェニルスルフォニル基等の置換スルフォニル基；シアノ基；フルオロ、クロロ、ブロモ、ヨード等のハロゲン基等が挙げられる。これらの中でも、アルキル基、アルコキシ基、アリール基、シクロアルキル基、シクロアルキル基、アリールオキシ基、アラルキル基、エチニル基、ハロゲン基が好ましい。尚、 R_4 は、これらの置換基に限定するものではない。また、これらの置換基はさらに置換基を有することがある。

【0041】

次に、一般式(4)におけるカルボン酸イオンは、2価の連結基であるXを有さない場合($n=0$)と有する場合($n=1$)とに分けられる。更に、2価の連結基であるXを有する場合($n=1$)、Xは、カルボニル基を有する場合及び有さない場合の2種類の形態に分けられる。このため一般式(4)におけるカルボン酸イオンは、さらに、カルボニル基を有さない下記一般式(5)とカルボニル基を有する一般式(6)とで表される。ユーロビウム錯体は、これらのカルボン酸イオンを配位子とする錯体構造のいずれもが使用することができる。

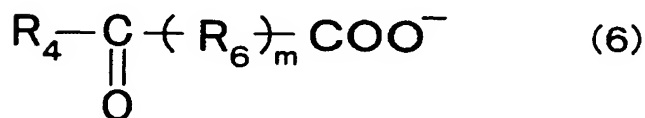
【0042】

【化6】



【0043】

【化7】



(13)

【0044】

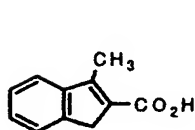
一般式(5)及び一般式(6)中、 R_6 は、2価の連結基となるものであればよいが、例えば、アルキレン基、環集合炭化水素から誘導される2価の連結基、脂肪族環、芳香族環、複素環から誘導される2価の連結基等が挙げられる。また、一般式(6)中、 m は0又は1である。 R_6 の、アルキレン基としては、メチレン、エチレン等が挙げられる。環集合炭化水素としては、ビフェニル、テルフェニル、ピナフチル、シクロヘキシルベンゼン、フェニルナフタレン等が挙げられる。脂肪族環としては、シクロペンタン、シクロヘキサン、シクロヘプタン、ノルボルナン、ビスシクロヘキシル等が挙げられる。芳香族環としては、前述した芳香族環の具体例と同様な化合物が挙げられる。複素環としては、前述した芳香族複素環の他に、ピラゾリン、ピペラジン、イミダゾリジン、モルホリン等の脂肪族複素環が挙げられる。その他、 $-SCH_2-$ 等のチオアルキレン； $-OCH_2-$ 等のオキシアルキレン；ビニレン($-C=C-$)等が挙げられる。尚、 R_6 は、これらの2価の置換基に限定するものではない。また、これらの2価の置換基はさらに置換基を有することがある。

【0045】

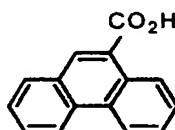
一般式(4)におけるカルボン酸イオンが誘導されるカルボン酸の具体例を以下に例示する。なお、本実施の形態において使用するカルボン酸は、これらに限定されるものではない。一般式(4)において n が0の場合の化合物は、以下のカルボン酸(1~10)が挙げられる。

【0046】

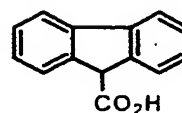
【化8】



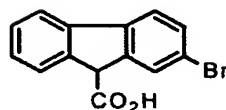
1



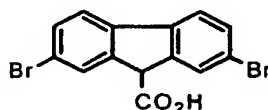
2



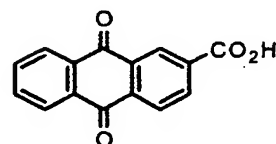
3



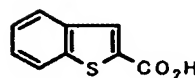
4



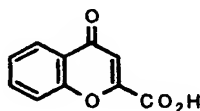
5



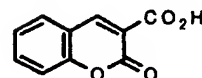
6



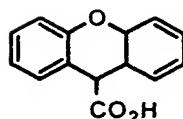
7



8



9



10

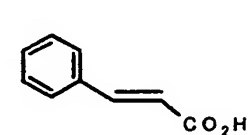
【0047】

(14)

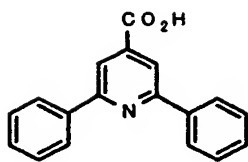
次に、一般式(4)においてnが1であり、XがR₆である場合(一般式(5))の化合物は、以下のカルボン酸(11~15)が挙げられる。

【0048】

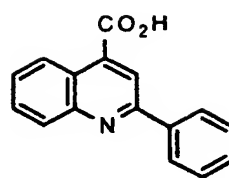
【化9】



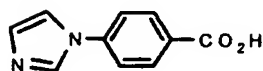
11



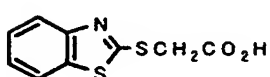
12



13



14



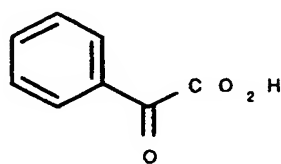
15

【0049】

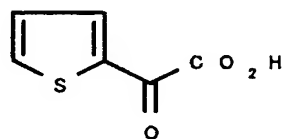
次に、一般式(6)において、mが0の場合の化合物は、以下のカルボン酸(16及び17)が挙げられる。

【0050】

【化10】



16



17

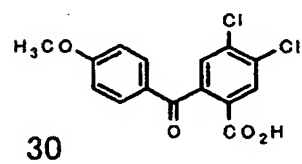
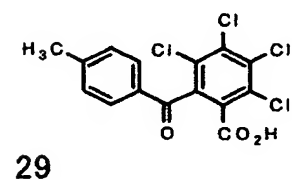
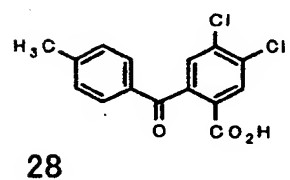
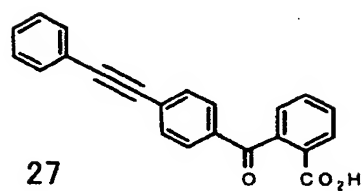
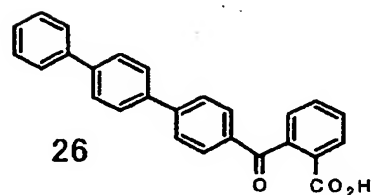
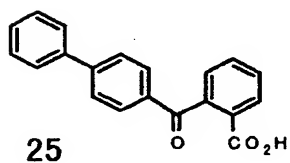
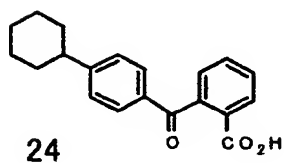
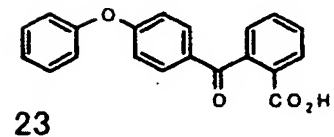
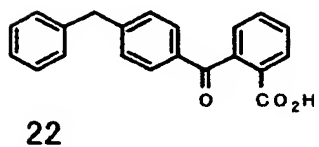
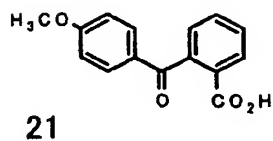
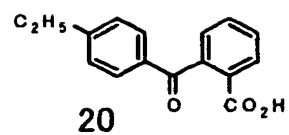
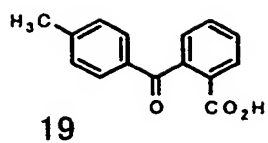
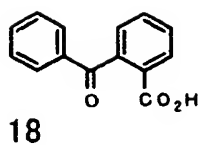
【0051】

一般式(6)において、mが1の場合であって、R₄がフェニル基、R₆がフェニル基の場合の化合物は、以下のカルボン酸(18~30)が挙げられる。

【0052】

【化11】

(15)



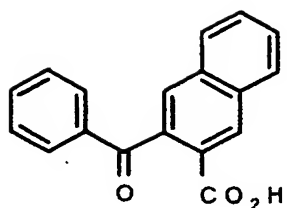
【0053】

一般式(6)において、 m が1の場合であって、 R_4 がフェニル基、 R_6 がナフチル基の場合の化合物は、以下のカルボン酸(31~34)が挙げられる。

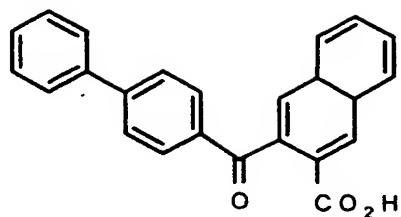
【0054】

【化12】

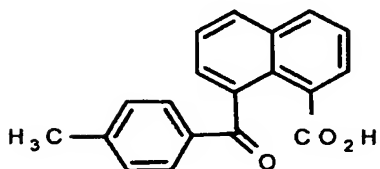
(16)



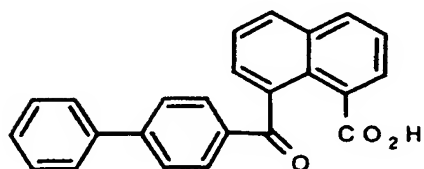
31



32



33



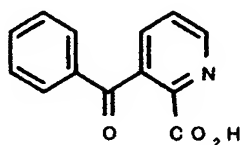
34

【0055】

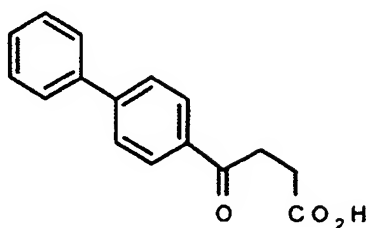
一般式(6)において、 m が1の場合であって、 R_4 がフェニル基、 R_6 がその他の基の場合の化合物は、以下のカルボン酸(35~37)が挙げられる。

【0056】

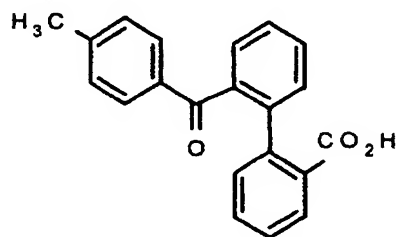
【化13】



35



36



37

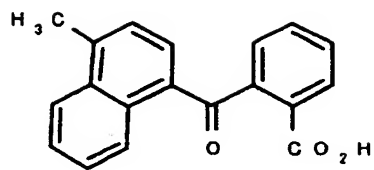
【0057】

一般式(6)において、 m が1の場合であって、 R_4 がナフチル基、 R_6 が芳香族環の場合の化合物は、以下のカルボン酸(38~41)が挙げられる。

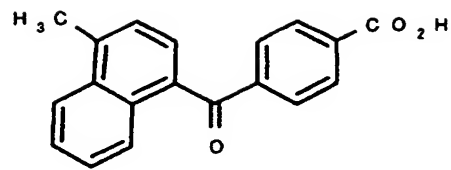
【0058】

【化14】

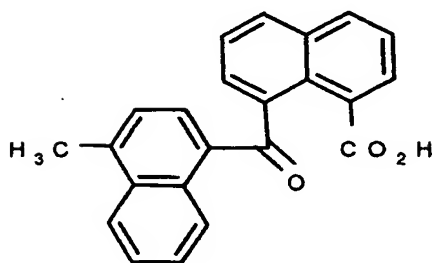
(17)



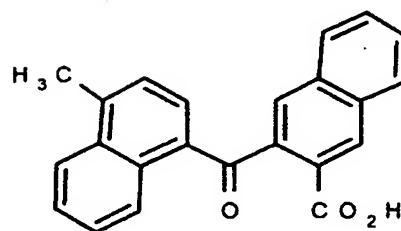
38



39



40



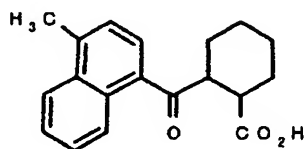
41

【0059】

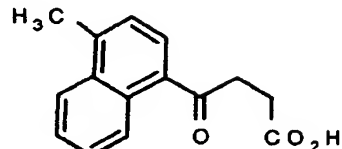
一般式(6)において、 m が1の場合であって、 R_4 がナフチル基、 R_6 がその他の基の場合の化合物は、以下のカルボン酸(42~44)が挙げられる。

【0060】

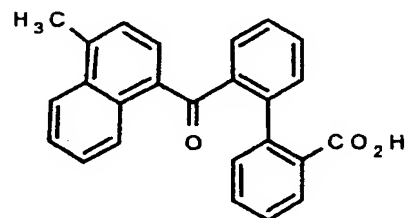
【化15】



42



43



44

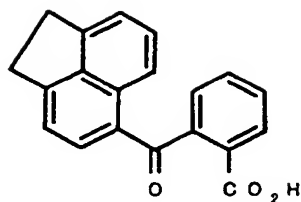
【0061】

一般式(6)において、 m が1の場合であって、 R_4 がアセナフチル基、 R_6 がフェニル基その他の場合の化合物は、以下のカルボン酸(45~48)が挙げられる。

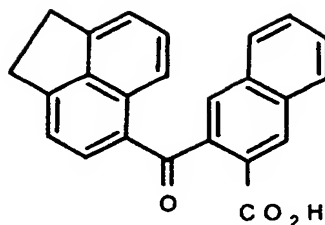
【0062】

【化16】

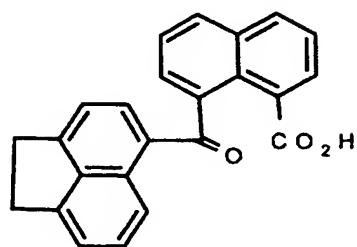
(18)



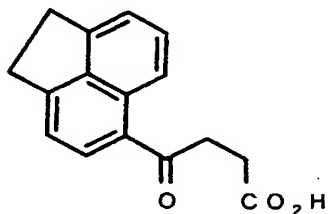
45



46



47



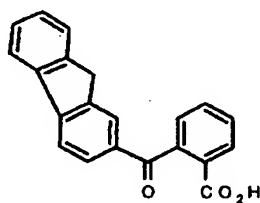
48

【0063】

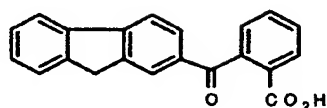
一般式(6)において、 m が1の場合であって、 R_4 がフルオレニル基、 R_6 がフェニル基の場合の化合物は、以下のカルボン酸(49～55)が挙げられる。

【0064】

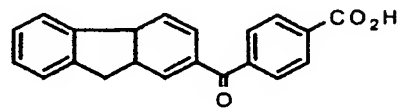
【化17】



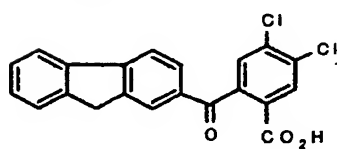
49



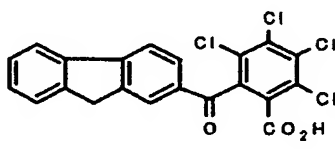
50



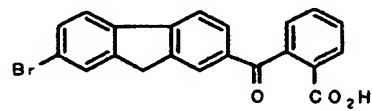
51



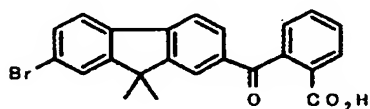
52



53



54



55

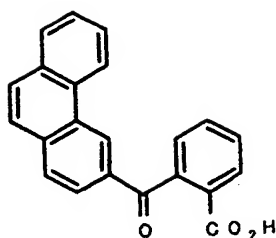
【0065】

一般式(6)において、 m が1の場合であって、 R_4 がフェナントレニル基、 R_6 がフェニル基その他の場合の化合物は、以下のカルボン酸(56～59)が挙げられる。

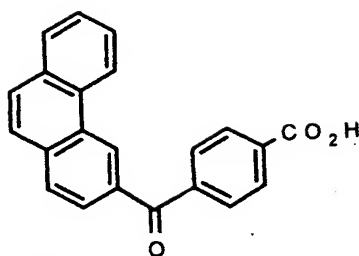
【0066】

【化18】

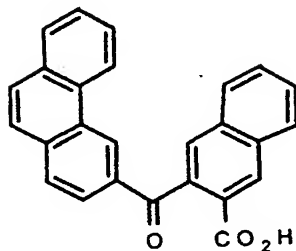
(19)



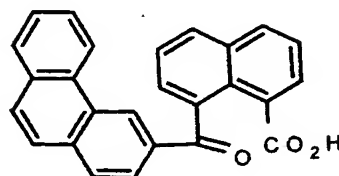
56



57



58

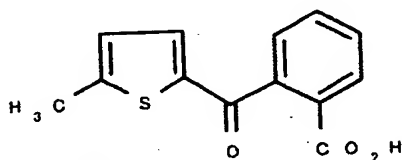


59

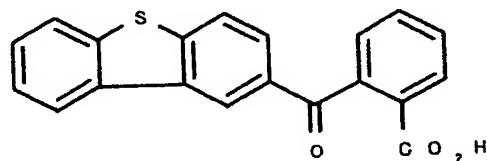
【0067】
一般式(6)において、 m が1の場合であって、 R_4 が複素環基、 R_6 がフェニル基の場合の化合物は、以下のカルボン酸(60及び61)が挙げられる。

【0068】

【化19】



60



61

【0069】
一般式(4)における配位子としてのカルボン酸イオンが誘導されるカルボン酸は、公知の合成方法により合成することが出来る。合成法については、例えば、新実験化学講座第14巻「有機化合物の合成と反応(II)」第921頁(1977)日本化学会編、又は、第4版実験化学講座第22巻「有機合成IV」第1頁(1992)日本化学会編等に記載されている。代表的な合成法としては、対応する第1アルコールやアルデヒドの酸化反応、エステルやニトリルの加水分解反応、酸無水物によるフリーデル・クラフツ反応等が挙げられる。

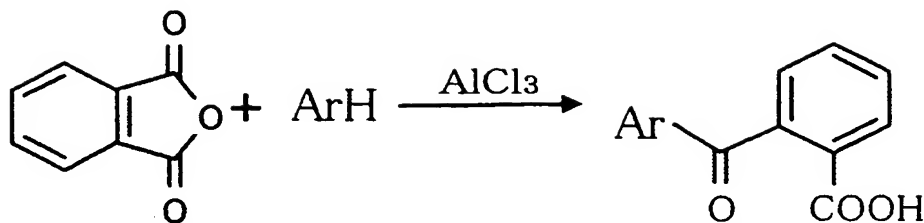
【0070】

特に、無水フタル酸、ナフタル酸無水物、無水こはく酸、ジフェン酸無水物、1,2-シクロヘキサジカルボン酸無水物、2,3-ピリダジジカルボン酸無水物等のジカルボン酸の環状無水物を用いたフリーデル・クラフツ反応では、分子内にカルボニル基を有するカルボン酸が合成できる。例えば、芳香族炭化水素又は芳香族複素環と無水フタル酸とを用いたフリーデル・クラフツ反応によれば、下記反応式に示すように、ベンゼン環のオルト位にカルボニル基が結合したカルボン酸が容易に合成できる。ベンゼン環のオルト位にカルボニル基が結合したカルボン酸は、パラ位置換体と比べ輝度が高い錯体が得られやすいことから好ましい。尚、式中、Arは、芳香族炭化水素又は芳香族複素環を表す。

【0071】

【化20】

(20)



【0072】

一般式(4)におけるルイス塩基からなる補助配位子(R₅)としては、前述した一般式(2)におけるルイス塩基からなる補助配位子(R₂)と同様な化合物が挙げられる。

【0073】

本実施の形態が適用される発光装置10において、蛍光体層12は、例えば、ユーロピウム錯体と、必要に応じて、他の希土類イオン錯体、その他の有機蛍光体、無機蛍光体を、適当なバインダー樹脂中に溶解又は分散させて混合した樹脂組成物として調製し、これを、外部キャップ13の内壁等の半導体発光素子11からの光を吸収する位置に塗布その他の方法により配置される。バインダー樹脂としては、通常、熱可塑性樹脂、熱硬化性樹脂、光硬化性樹脂等が挙げられる。具体的には、例えば、ポリメタアクリル酸メチル等のメタアクリル樹脂；ポリスチレン、スチレン-アクリロニトリル共重合体等のスチレン系樹脂；ポリカーボネート樹脂；ポリエステル樹脂；フェノキシ樹脂；ブチラール樹脂；ポリビニルアルコール；エチルセルロース、セルロースアセテート、セルロースアセテートブチレート等のセルロース系樹脂；エポキシ樹脂；フェノール樹脂；シリコン樹脂等が挙げられる。

【0074】

本実施の形態が適用される発光装置10は、ユーロピウム錯体等の希土類イオン錯体を含有する赤色蛍光体と共に、さらに、青色蛍光体と緑色蛍光体と備え、これらを組み合わせることにより、白色光を発光することが出来る。尚、必要に応じて、その他の有機赤色蛍光体、無機赤色蛍光体を含有する蛍光体を含んでもよい。青色蛍光体又は緑色蛍光体としては、公知の蛍光体を使用することが出来る。例えば、青色蛍光体としては、ZnS:Ag、Sr₅(PO

4)₃Cl:Eu、BaMgAl₁₀O₁₇:Eu等の無機蛍光体が挙げられる。また、緑色蛍光体としては、ZnS:Cu、ZnS:CuAl、BaMgAl₁₀O₁₇:Eu、Mn等の無機蛍光体が挙げられる。また、このほかに青色蛍光体としてはトリウム錯体が、緑色蛍光体としてはテルビウム錯体等の有機蛍光体が挙げられる。これらの錯体の配位子としては、公知の配位子の他に、本実施の形態におけるユーロピウム錯体の配位子として使用されるβ-ジケトンアニオンや芳香族基を含むカルボン酸イオンを用いることが出来る。

【0075】

白色光を発光させるには、例えば、赤色蛍光体と青色蛍光体及び緑色蛍光体の混合物を含む蛍光体樹脂層を外部キャップ13の内側に塗布して蛍光体層12を形成する方法、又は、この蛍光体樹脂層を半導体発光素子11上に配置すればよい。この場合、赤色蛍光体は、青色蛍光体、緑色蛍光体とは必ずしも同一の樹脂中に混合されなくてもよく、青色蛍光体と緑色蛍光体を含有する樹脂層の上に赤色蛍光体を含有する樹脂層が積層されていてもよい。

【0076】

次に、本発明が適用される発光装置の他の実施の形態について説明する。図2は、第2の実施の形態における発光装置を説明するための図である。ここには、半導体発光素子上に、無機蛍光体を含む樹脂層と錯体を含む蛍光体層とが順次積層されている。図2に示された発光装置20は、ブラケット28と、ブラケット28の上部を覆い、ガラス等で形成された外部キャップ23と、ブラケット28に取り付けられたマウントリード26b及びインナーリード26aと、マウントリード26b及びインナーリード26aと導通す

(21)

る電気接点29と、マウントリード26b上部のカップ内に収納された半導体発光素子21と、マウントリード26b上部のカップ内に充填された無機蛍光体層27と、希土類イオン錯体等がバインダー樹脂中に混合分散された蛍光体層22と、導電性ワイヤ25a及び導電性ワイヤ25bと、を有し、外部キャップ23の内部は、真空又は窒素ガス、アルゴンガス等の不活性ガス24が充填されている。

【0077】

尚、半導体発光素子が発光することにより発生する熱の影響を緩和することにより、蛍光性錯体の耐久性をさらに向上させることができる。例えば、半導体発光素子と空間を隔て又は断熱層、光拡散層等の他の層を介して蛍光性錯体を含有する蛍光体層を設ける方法、耐熱性の高い無機蛍光体層と蛍光性錯体を含有する蛍光体層を積層する方法等が挙げられる。これにより、一般的に無機蛍光体に比べ、耐熱性に劣る有機材料からなる錯体を含む蛍光体の熱劣化を抑えることができ、耐久性に優れた発光装置を得ることができる。

【0078】

例えば、図2に示された発光装置20のように、蛍光体が半導体発光素子21に近接して配置される場合は、無機蛍光体からなる層と錯体を含む蛍光体の層がそれぞれ分離された積層体であることが好ましく、無機蛍光体層が発光素子に近い方の層であることが好ましい。つまり、半導体発光素子21と錯体を含む蛍光体層22との間に無機蛍光体を含む無機蛍光体層27を配置することにより、半導体発光素子21の発光により発生する熱が蛍光体層22を局所的に加熱することを緩和することができる。また、LEDの一般的な形態である砲弾型形状の場合には、エポキシ樹脂等の封止樹脂中に蛍光体を混合することもできる。この場合は、蛍光体からの光はより拡散された光となる。

【0079】

本実施の形態が適用される発光装置10及び発光装置20は、単独で、又は複数個を組み合わせることにより、種々の照明装置として使用することができる。照明装置としては、例えば、照明ランプ、液晶パネル用バックライト、超薄型照明等が挙げられる。

【0080】

【実施例】

以下に実施例を挙げて、本実施の形態を、より具体的に説明する。尚、本実施の形態は、実施例に限定されるものではない。また、実施例中の部及び%は、特に断らない限り総て重量基準である。

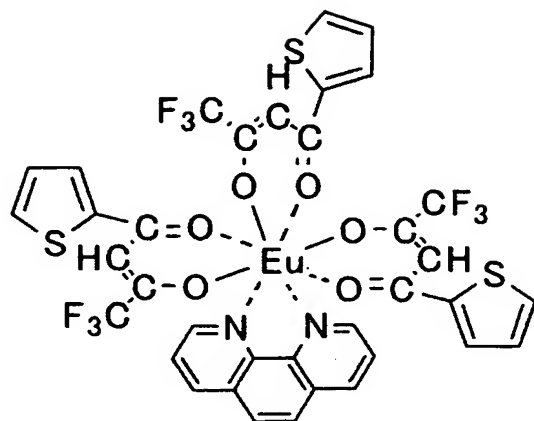
(実施例1～2、比較例)

下記式で示されるβ-ジケトン配位子とするユーロピウム(Eu)錯体10部と、ポリビニルブチラール(積水化学社製 エスレックBL-1)のメチルエチルケトン溶液(濃度20%)200部とを混合して混合溶液を調製し、この混合溶液0.2～0.3gを直径14mmのガラスアンプル内部に塗布し乾燥して蛍光体の被膜を形成した。次に、このアンプルを、表1に示した条件((1)真空封止(2.5×10⁻⁵トール)、(2)窒素ガス封入(酸素濃度20ppm以下)、(3)空気封入(酸素濃度約20%))で処理し、Eu錯体を含有する蛍光体の被膜が内面に塗布されたガラスアンプルを作成した。次に、このガラスアンプルを、耐光試験機(アトラス社製Ci4000)を用いて、紫外から可視領域迄の光を、40時間、それぞれ照射し、その後、ユーロピウム(Eu)錯体を含有する蛍光体の蛍光強度を、日立蛍光分光測定器F4500を用いて測定した。蛍光体の蛍光強度は、耐光試験機による光を照射しない場合の蛍光強度を100とした指数として表す。数値が100に近いほど、耐光性が良好である。結果を表1に示す。

【0081】

【化21】

(22)



【0082】

【表1】

	実施例		比較例
	1	2	
	真空	窒素ガス	空気
光照射時間 0	100	100	100
40時間	90	82	0.3

【0083】

表1の結果から、真空状態に置かれた蛍光体に光を照射する場合（実施例1）及び窒素ガス雰囲気下に置かれた蛍光体に光を照射する場合（実施例2）は、いずれも、蛍光体の耐光性が良好であり、耐久性が向上することが分かる。これに対して、空気中に置かれた蛍光体に光を照射すると（比較例）、40時間後に30%迄に低下し、耐光性が著しく不良であることが分かる。

【0084】

【発明の効果】

かくして本発明によれば、蛍光性錯体を含有する蛍光体の耐久性を向上させ、高強度の発光を発生させることのできる発光装置、それを使用した照明装置が提供される。

【図面の簡単な説明】

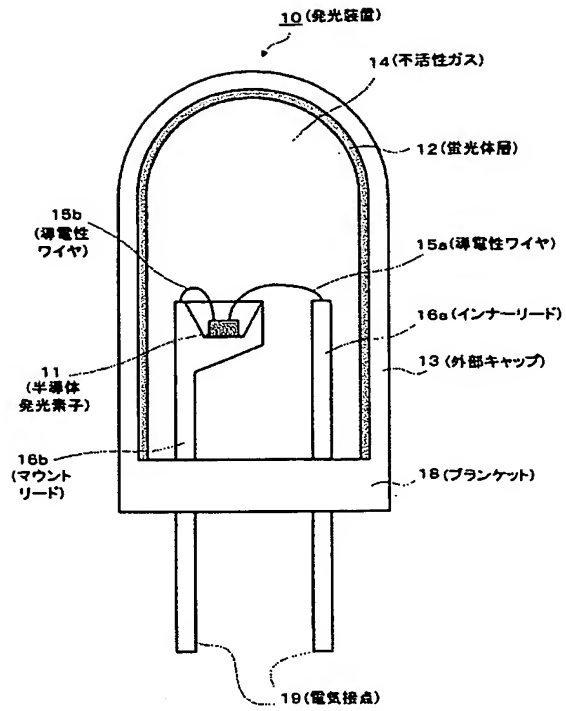
【図1】本実施の形態が適用される発光装置を説明するための図である。

【図2】第2の実施の形態の発光装置を説明するための図である。

【符号の説明】

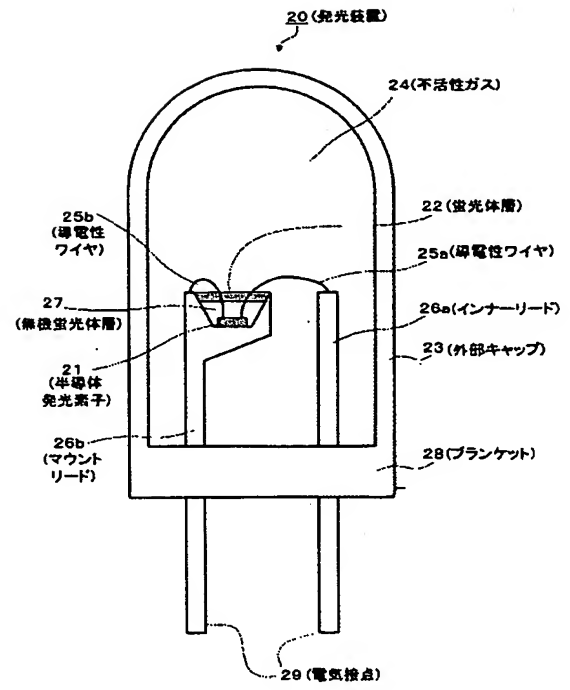
10, 20…発光装置、11, 21…半導体発光素子、12, 22…蛍光体層、13, 23…外部キャップ、14, 24…不活性ガス、15a, 15b, 25a, 25b…導電性ワイヤ、16a, 26a…インナーリード、16b, 26b…マウントリード、18, 28…ブラケット、19, 29…電気接点、27…無機蛍光体層

【図 1】



(23)

【図 2】



(24)

フロントページの続き

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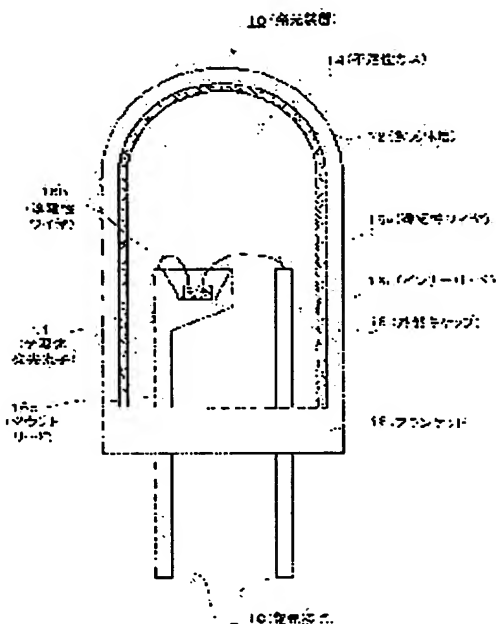
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(54) LIGHT EMITTING DEVICE AND LIGHTING DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a light emitting device that can improve the durability of a fluorescent body and generate a highly luminescent light, and a lighting device using the same.

SOLUTION: The light emitting device 10 is provided with a blanket 18, an external cap 13 that is made of light transmission material such as glass or the like and is formed like a dome over an upper part of the blanket 18, a mount lead 16b and an inner lead 16a that are fitted to the blanket 18, an electric contact 19 that is provided on the bottom of the blanket 18 and is electrically connected with the mount lead 16b and the inner lead 16a, a semiconductor light emitting part 11 that is housed in a cup at the upper side of the mount lead 16b, a film-like fluorescent layer 12 coated on the inside of the external cap 13, a conductive wire 15a connecting electrically the inner lead 16a and the semiconductor light emitting part 11, and a conductive wire 15b connecting electrically the semiconductor light emitting part 11 and the mount lead 16b. The inside of the external cap 13 is in vacuum or filled with an inert gas 14 such as nitrogen gas, argon gas, etc.



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CLAIMS

[Claim(s)]

[Claim 1]

The light emitting device which emits light in the light from near-ultraviolet light to a light field, It has a fluorescent substance containing at least one sort of fluorescence complexes which emit light by the light from said light emitting device,

Luminescence equipment characterized by putting said fluorescent substance on the bottom of a hypoxia concentration ambient atmosphere.

[Claim 2]

Said light emitting device is luminescence equipment according to claim 1 characterized by being the semi-conductor light emitting device which emits light in the light which has peak wavelength in the range of 360 to 470nm.

[Claim 3]

Luminescence equipment according to claim 1 or 2 characterized by installing said fluorescent substance in the interior of the container formed with the light transmission nature ingredient.

[Claim 4]

Luminescence equipment according to claim 3 with which said interior of a container is characterized by being a container inner surface.

[Claim 5]

Said fluorescent substance is claim 1 characterized by putting the oxygen density on the bottom of an ambient atmosphere 100 ppm or less thru/or luminescence equipment given in 4 any 1 terms.

[Claim 6]

Said fluorescent substance is claim 1 characterized by being put on the bottom of a vacuum or the ambient atmosphere of inert gas thru/or luminescence equipment given in 5 any 1 terms.

[Claim 7]

Claim 1 characterized by choosing said fluorescence complex from a rare earth ion complex thru/or luminescence equipment given in 6 any 1 terms.

[Claim 8]

Luminescence equipment according to claim 7 characterized by choosing said rare earth ion complex from the rare earth ion complex which makes a ligand the anion guided from the carboxylic acid which has a substituent containing beta-diketone or the aromatic series ring which has a substituent containing an aromatic series ring.

[Claim 9]

Said rare earth ion complex is luminescence equipment according to claim 7 or 8 characterized by making a Lewis base into an auxiliary ligand.

[Claim 10]

Said rare earth ion complex is claim 7 characterized by being the europium complex which emits light in red by the light from said light emitting device thru/or luminescence equipment given in 9 any 1 terms.

[Claim 11]

Said fluorescent substance is claim 1 characterized by being the resin constituent which was made to dissolve or distribute said fluorescence complex, and was mixed thru/or luminescence equipment given in 10 any 1 terms.

[Claim 12]

Claim 1 characterized by having further the blue fluorescent substance and green fluorescent substance which emit light by the light from said light emitting device thru/or luminescence equipment given in 11 any 1 terms.

[Claim 13]

Claim 3 characterized by preparing a light emitting device in the interior of a container, and establishing space in said light emitting device and fluorescent substance inside said container through a partition or other layers thru/or luminescence equipment given in 12 any 1 terms.

[Claim 14]

Said fluorescent substance is claim 3 characterized by being prepared in the interior of said container through said light emitting device and optical diffusion layer thru/or luminescence equipment given in 13 any 1 terms.

[Claim 15]

Said fluorescent substance is luminescence equipment according to claim 1 to 14 characterized by being the layered product of the layer which consists of an inorganic fluorescent substance, and the layer which consists of a fluorescent substance containing said fluorescence complex.

[Claim 16]

The lighting system characterized by having claim 1 thru/or luminescence equipment given in 15 any 1 terms.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the luminescence equipment with which the endurance of a fluorescent substance was improved, and the lighting system which used this in more detail about luminescence equipment and a lighting system.

[0002]

[Description of the Prior Art]

Conventionally, the luminescence equipment which carried out color conversion of the light of a discharge lamp or a semi-conductor light emitting device with the fluorescent substance is used for lighting etc. These luminescence equipments mix blue, red, and green light, and many examination is made in order to make the light of various colors of white and others emit light with color rendering properties uniform and sufficient in the large color reproduction range. The luminescence equipment which used semi-conductor light emitting devices, such as light emitting diode (LED) and semiconductor laser (LD), especially has high luminous efficiency, there is also an advantage of the environmental cure side of not using mercury, and development of the luminescence equipment which combined LED, LD, and a fluorescent substance is performed briskly.

[0003]

the fluorescent lamp with which inorganic red fluorescent substances, such as Y₂O₃:Eu, are used especially for the luminescence equipment used combining LED, LD, and the organic red fluorescent substance containing the europium (Eu) complex which makes the anion of beta-diketone a ligand — comparing — the light of near-ultraviolet light to the light — efficient — absorbing — high — it is reported as equipment which can obtain brightness luminescence (for example, patent reference 1 and patent reference 2 reference).

[0004]

[Patent reference 1]

JP,10-12925,A

[Patent reference 2]

** table No. 509912 [2000 to] official report

[0005]

[Problem(s) to be Solved by the Invention]

By the way, it is known that it will be easy to carry out photodegradation of the fluorescence complexes, such as a rare earth ion complex used for such an organic red fluorescent substance etc., and development of LED or LD is turned in the direction which emits light in the light of short wavelength more in recent years. Consequently, degradation of a fluorescent substance, a sealing agent, etc. with which a large light in energy was irradiated became remarkable, and, for this reason, the need for utilization of luminescence equipment that endurance is required has arisen.

[0006]

This invention is made that the problem which was thrown into relief when developing the luminescence equipment which uses such a fluorescence complex should be solved. Namely, the object of this invention raises substantially the endurance of the fluorescent substance containing fluorescence complexes, such as rare earth ion complexes including the europium complex which is excellent in a luminescence property, and aims at offering the luminescence equipment which can be made to generate luminescence of high intensity, and the lighting system which used it.

[0007]

[Means for Solving the Problem]

That luminescence equipment with high endurance should be offered, when this invention person etc. considered photodegradation of fluorescence complexes, such as an europium complex, under various conditions, he found out that the lightfastness of a fluorescence complex improved under the reduced pressure to which it became clear that oxygen participates in photodegradation and it lowered the oxygen density, or in inert gas, such as nitrogen gas and an argon. That is, the luminescence equipment with which this invention is applied is equipped with the light emitting device which emits light in the light from near-ultraviolet light to a light field, and the fluorescent substance containing at least one sort of fluorescence complexes which emit light by the light from this light emitting device, and is characterized by putting the fluorescent substance on the bottom of a hypoxia concentration ambient atmosphere.

[0008]

the luminescence equipment which uses an inorganic red fluorescent substance by combining this light emitting device and a fluorescence complex with the range of 360 to 470nm using the semi-conductor light emitting device which emits light in the light which has peak wavelength as a light emitting device used for the luminescence equipment with which this invention is applied — comparing — high — brightness luminescence can be obtained. Moreover, the light of the light is [installing the fluorescent substance containing a fluorescence complex in the interior of the container formed with the light transmission nature ingredient] efficiently absorbable from the description, then near-ultraviolet light.

[0009]

Furthermore, the lightfastness of the fluorescent substance used for the luminescence equipment with which this invention is applied of the description, then the fluorescence complex contained in a fluorescent substance improves notably that the oxygen density is put on the bottom of an ambient atmosphere 100 ppm or less. Moreover, in order for the oxygen density on which a fluorescent substance is put to consider as the bottom of an ambient atmosphere 100 ppm or less, it is desirable that it is under a vacuum or the ambient atmosphere of inert gas.

[0010]

- Moreover, as for the fluorescence complex contained in the fluorescent substance used for the luminescence equipment with which this invention is applied, it is desirable to be chosen out of a rare earth ion complex. As for especially the fluorescent substance used for the luminescence equipment with which this invention is applied, it is desirable that it is characterized by containing the fluorescence complex chosen from the rare earth ion complex which makes a ligand the anion guided from the carboxylic acid which has a substituent containing beta-diketone or the aromatic series ring which has a substituent containing an aromatic series ring. Moreover, as for a rare earth ion complex, it is desirable from the point of the improvement in brightness to make a Lewis base into an auxiliary ligand.
- Especially, as for a rare earth ion complex, it is desirable that it is an europium complex.

[0011]

It is desirable that it is the resin constituent which was made to dissolve or distribute a fluorescence complex and was mixed as a mode of this fluorescent substance. Moreover, the luminescence equipment with which this invention is applied can use as the description, then white luminescence equipment to have further the blue fluorescent substance and green fluorescent substance which emit light by the light from a light emitting device with the fluorescent substance which emits light in red by the light from light emitting devices, such as an europium complex.

[0012]

The container with which the luminescence equipment with which this invention is applied was formed the light transmission nature ingredient on the other hand, and the interior was maintained at the hypoxia concentration ambient atmosphere. If characterized by having the fluorescent substance in which it was prepared in the interior of this container, and the light emitting device which emits light in the light from near-ultraviolet light to a light field, a light emitting device, and space were established inside the container through a partition or other layers It can excel in endurance and can grasp as luminescence equipment of one apparatus which can generate luminescence of high intensity.

[0013]

In this case, as for a fluorescent substance, it is desirable to be prepared in the interior of the container maintained at the hypoxia concentration ambient atmosphere through the light emitting device and the optical diffusion layer.

- Moreover, a fluorescent substance may mix an inorganic fluorescent substance and the fluorescent substance containing a fluorescence complex, when using it with an inorganic fluorescent substance. Furthermore, when a fluorescent substance approaches a semi-conductor light emitting device and is arranged, it is desirable that the layer which consists of an inorganic fluorescent substance, and the layer which consists of a fluorescent substance containing a fluorescence complex are the layered products separated, respectively.

[0014]

And a lighting system equipped with the luminescence equipment with which this invention is applied can be offered.

[0015]

[Embodiment of the Invention]

The luminescence equipment with which the gestalt of this operation is applied is equipped with the light emitting device which emits light in the light from near-ultraviolet light to a light field, and the fluorescent substance containing at least one sort of fluorescence complexes which emit light by the light from this light emitting device, and the fluorescent substance is put on the bottom of a hypoxia concentration ambient atmosphere. The endurance of the bottom of a hypoxia concentration ambient atmosphere of a fluorescence complex improves here by being a thing under the ambient atmosphere where an oxygen density is low, and putting a fluorescent substance on the bottom of such an ambient atmosphere from air. Although it becomes the bottom of a hypoxia concentration ambient atmosphere making it reduced pressure or a vacuum or by considering as the bottom of the ambient atmosphere of inert gas, in order to raise the lightfastness of a fluorescence complex more, it is desirable that an oxygen density is 1000 ppm or less.

Next, the luminescence equipment with which the gestalt of this operation is applied is explained. Drawing 1 is drawing for explaining the luminescence equipment in the gestalt of this operation. The external cap 13 with which the luminescence equipment 10 shown in drawing 1 was formed in the dome mold light transmission nature ingredients, such as a bonnet, for example, glass etc., in the upper part of a blanket 18 and a blanket 18, Mounting lead 16b and inner lead 16a which were attached in the blanket 18, Electric contact 19 which is attached in the lower part of a blanket 18 and flows with mounting lead 16b and inner lead 16a, The semi-conductor light emitting device 11 contained in the cup of the mounting lead 16b upper part, The fluorescent substance layer 12 of the coat which it filled up in the cup of the mounting lead 16b upper part, and mixed distribution of the red fluorescent substance was carried out into binder resin, and was applied inside the external cap 13, Conductive wire 15a which flows through inner lead 16a and the semi-conductor light emitting device 11, It has conductive wire 15b which flows through the semi-conductor light emitting device 11 and mounting lead 16b, and, as for the interior of the external cap 13, fills up with inert gas 14, such as a vacuum or nitrogen gas, and argon gas.

[0016]

The semi-conductor light emitting device 11 emits light in the light from near-ultraviolet light to a light field, and the fluorescent substance contained in the fluorescent substance layer 12 absorbs this light, and it emits light in the light of long wavelength more. Instead of filling up the interior of the external cap 13 with nitrogen gas, it is also possible by maintaining at a vacua to raise the lightfastness of the fluorescent substance layer 12 and to raise the endurance of luminescence equipment 10. Although the relation between the oxygen density in the interior of the external cap 13 and the degradation behavior of the fluorescence complex contained in the fluorescent substance layer 12 containing a fluorescence complex is not clear, if light is preferably irradiated from the semi-conductor light emitting device 11 under an ambient atmosphere 20 ppm or less, lightfastness will improve a fluorescence complex remarkably 100 ppm or less of oxygen densities. Moreover, lightfastness improves under low humidity.

[0017]

As a semi-conductor light emitting device 11, the laser diode (LD) or light emitting diode (LED) which has the peak wavelength of an emission spectrum in the range of 360 to 470nm is used. Especially as such a laser diode (LD) or light emitting diode (LED), although not limited, LD and LED which have peak wavelength from 380nm to 470nm, for example are desirable. Since organic compounds, such as a complex and resin, tend to carry out [tend] photodegradation of the semi-conductor light emitting device which has peak wavelength in a short wavelength side too much, it is not desirable. Moreover, when peak wavelength is in a long wavelength side too much, since the triplet energy level of the

ligand of an europium complex becomes low and the width of face of selection of the ligand which can emit light becomes narrow, it is not desirable.

[0018]

The fluorescent substance layer 12 is formed with the gestalt of the coat formed of spreading inside the external cap 13 in the resin constituent which consists of a fluorescence complex and resin. Especially as a fluorescence complex, although not limited, the rare earth ion complex which is a complex of one sort or two sorts or more of ligand anions and the ion of trivalent rare earth elements is usually used. Sm, Eu, Tb, Dy, Tm, etc. are mentioned as rare earth elements. Especially, as a red fluorescent substance, as Eu (europium) element and a blue fluorescent substance, the ion complex of Tb (terbium) element is used, and is used as Tm (thulium) element and a green fluorescent substance. In addition, in the fluorescent substance layer 12, it is also possible to use together suitably the organic fluorescent substance of others besides a rare earth ion complex and an inorganic fluorescent substance.

[0019]

An europium complex is desirable as a red fluorescent substance which emits light in high brightness in a difficult near-ultraviolet light exposure especially also in a rare earth ion complex with an inorganic fluorescent substance. Moreover, as for a rare earth ion complex, it is desirable that it is the complex which makes a ligand the carboxylic-acid ion which has a substituent containing the anion or aromatic series radical of beta-diketone which has a substituent containing an aromatic series ring. Hereafter, although an europium complex is mentioned as an example and explained as a rare earth ion complex, it is not restricted to this.

[0020]

As a complex which makes a ligand the anion of beta-diketone which has a substituent containing an aromatic series ring, the europium complex expressed with any one formula of the following general formula (1), (2), and the (3) is mentioned, for example.

(R1)3Eu (1)

(R1)3Eu(R2)2 (2)

[(R1) 4Eu] -R3+ (3)

(R1 is the anion of beta-diketone which has a substituent containing an aromatic series ring among a formula (1), (2), and (3), R2 is an auxiliary ligand which consists of a Lewis base, and + is the R3 4th class ammonium ion.)

[0021]

As beta-diketone which has a substituent containing the aromatic series ring in a formula (1), (2), and (3) If the substituent and beta-diketone containing an aromatic series ring are included in the structure, the connection approach Although it may be direct or you may connect by the divalent radical, what the direct aromatic series ring has connected with one [at least] ketone is desirable. It is desirable to have at least one aromatic series radical, and the aromatic hydrocarbon compound or aromatic heterocycle compound which may have a substituent is further mentioned as this aromatic series radical. As an aromatic hydrocarbon compound, benzene, naphthalene, a phenanthrene, a fluorene, etc. are mentioned, for example. As an aromatic heterocycle compound, the heterocyclic compound containing oxygen, such as a furan, a thiophene, pyrazoline, a pyridine, benzothiophene, a carbazole, a dibenzofuran, and a dibenzo thiophene, nitrogen, and a sulfur atom is mentioned.

[0022]

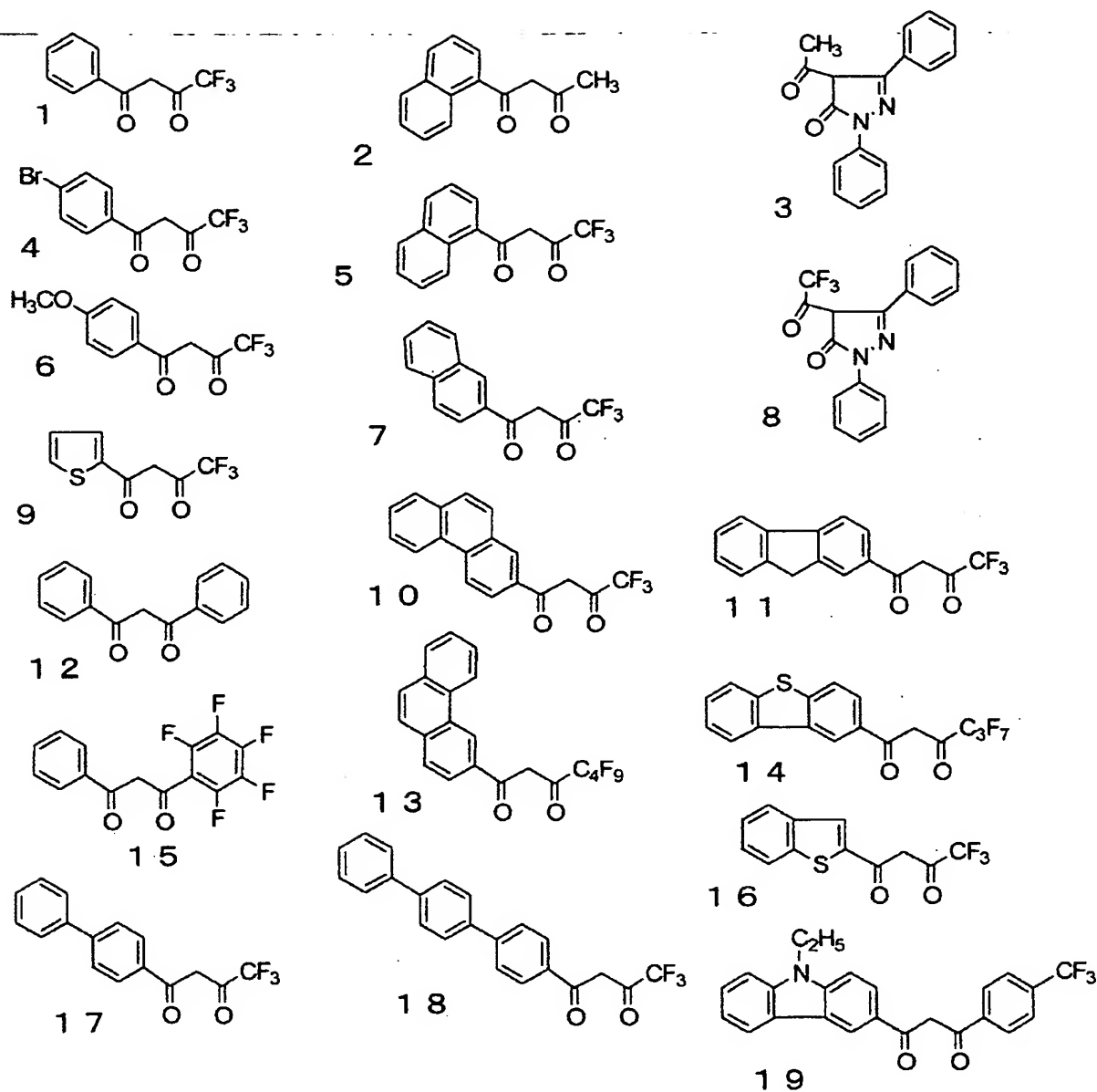
moreover, as a substituent of these aromatic hydrocarbon compounds or an aromatic heterocycle compound For example, alkyl groups, such as methyl, ethyl, propyl, and butyl; Trifluoromethyl, Fluoro alkyl groups, such as pentafluoro ethyl; Methoxy, the alkoxy group; phenyl of ethoxy **, Aryl groups, such as a naphthyl group; Aryloxy group; hydroxyl; allyl group; acetyls, such as benzyl and phenethyl, Acyl groups, such as a propionyl; Acyloxy radical; methoxycarbonyls, such as acetoxy, propionyloxy, and benzoyloxy one, alkoxy carbonyl group [, such as ethoxycarbonyl,]; — aryloxy carbonyl group [, such as phenoxy carbonyl]; — carboxyl group; — carbamoyl group; — amino-group; — dimethylamino — Permutation amino groups, such as diethylamino, methylbenzyl amino, diphenylamino, and acetyl methylamino; A methylthio, Permutation sulfonyl radical; cyano groups, such as permutation thio radical; sulfhydryl group; ethyl sulfonyls, such as ethyl thio, phenylthio, and benzyl thio, and phenyl sulfonyl; halogen radicals, such as fluoro, chloro, BUROMO, and iodine, etc. are mentioned. It may join together mutually and these substituents may form a ring.

[0023]

As substituents other than the aromatic series radical which constitutes beta-diketone, the substituent of the aromatic hydrocarbon compound mentioned above or an aromatic heterocycle compound and the same substituent (however, a halogen radical is removed) are mentioned. The example (1-19) of beta-diketone which has a substituent containing an aromatic series ring is shown below. In addition, in the gestalt of this operation, it is not limited to these.

[0024]

[Formula 1]

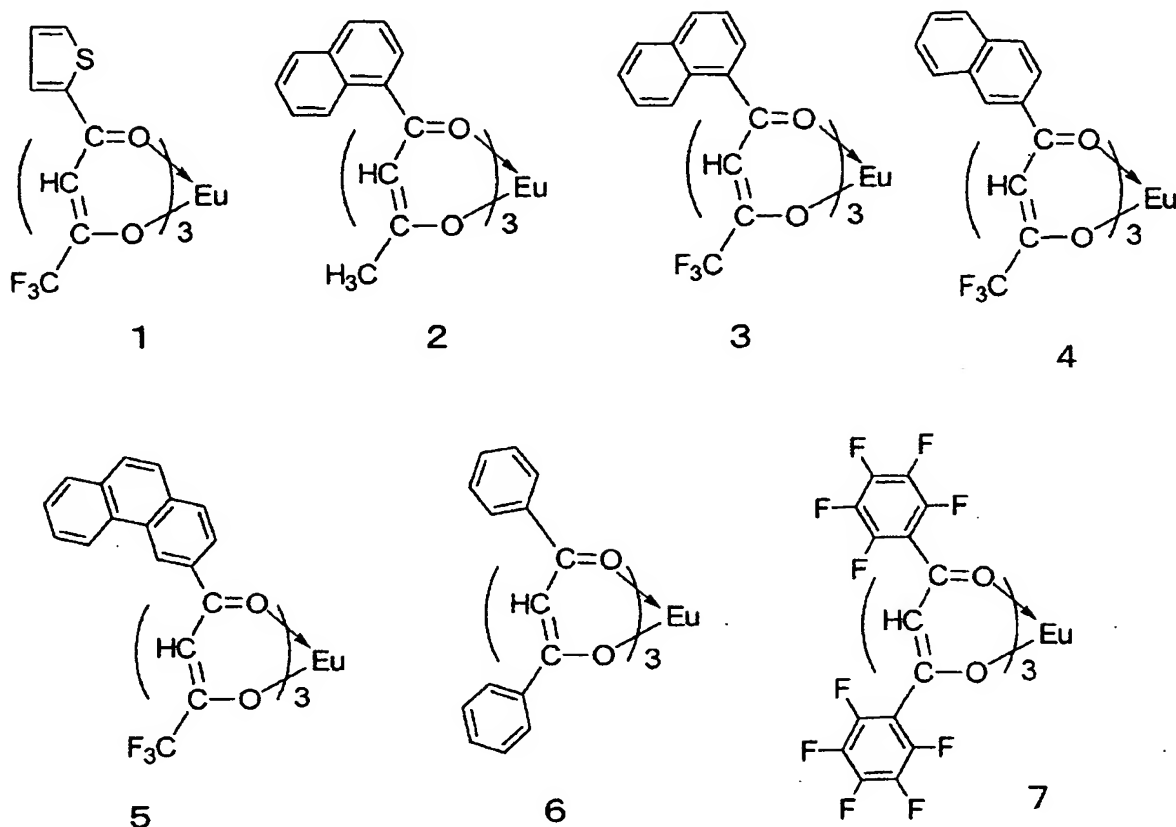


[0025]

The example (1-7) of an europium complex expressed with a general formula (1) is shown below. In addition, in the gestalt of this operation, it is not limited to these.

[0026]

[Formula 2]



[0027]

Next, the europium complex expressed with a general formula (2) is explained. It is chosen from the Lewis base compound which usually has the nitrogen atom or oxygen atom which can be configured to europium ion although not limited especially as an auxiliary ligand (R2) which consists of a Lewis base in a general formula (2). As those examples, the amine which may have a substituent, an amine oxide, phosphine oxide, a sulfoxide, etc. are mentioned. A compound different, respectively is sufficient as two Lewis base compounds used as an auxiliary ligand, and they may form one compound with two compounds.

[0028]

Specifically as an amine, a pyridine, pyrazine, quinoline, isoquinoline, phenanthridine, 2, and 2'-bipyridine, 1, 10-phenanthroline, etc. are mentioned. As an amine oxide, N-oxide of the above-mentioned amines, such as pyridine N-oxide, 2, 2'-bipyridine-N, and N'-dioxide, is mentioned. As phosphine oxide, triphenylphosphine oxide, trimethyl phosphine oxide, trioctyl phosphine oxide, etc. are mentioned. A diphenyl sulfoxide, a dioctyl sulfoxide, etc. are mentioned as a sulfoxide. The substituent mentioned above is illustrated as a substituent permuted by these. An alkyl group, an aryl group, an ARUKOSHIKIRU radical, an aralkyl radical, an aryloxy group, a halogen radical, etc. are desirable especially.

[0029]

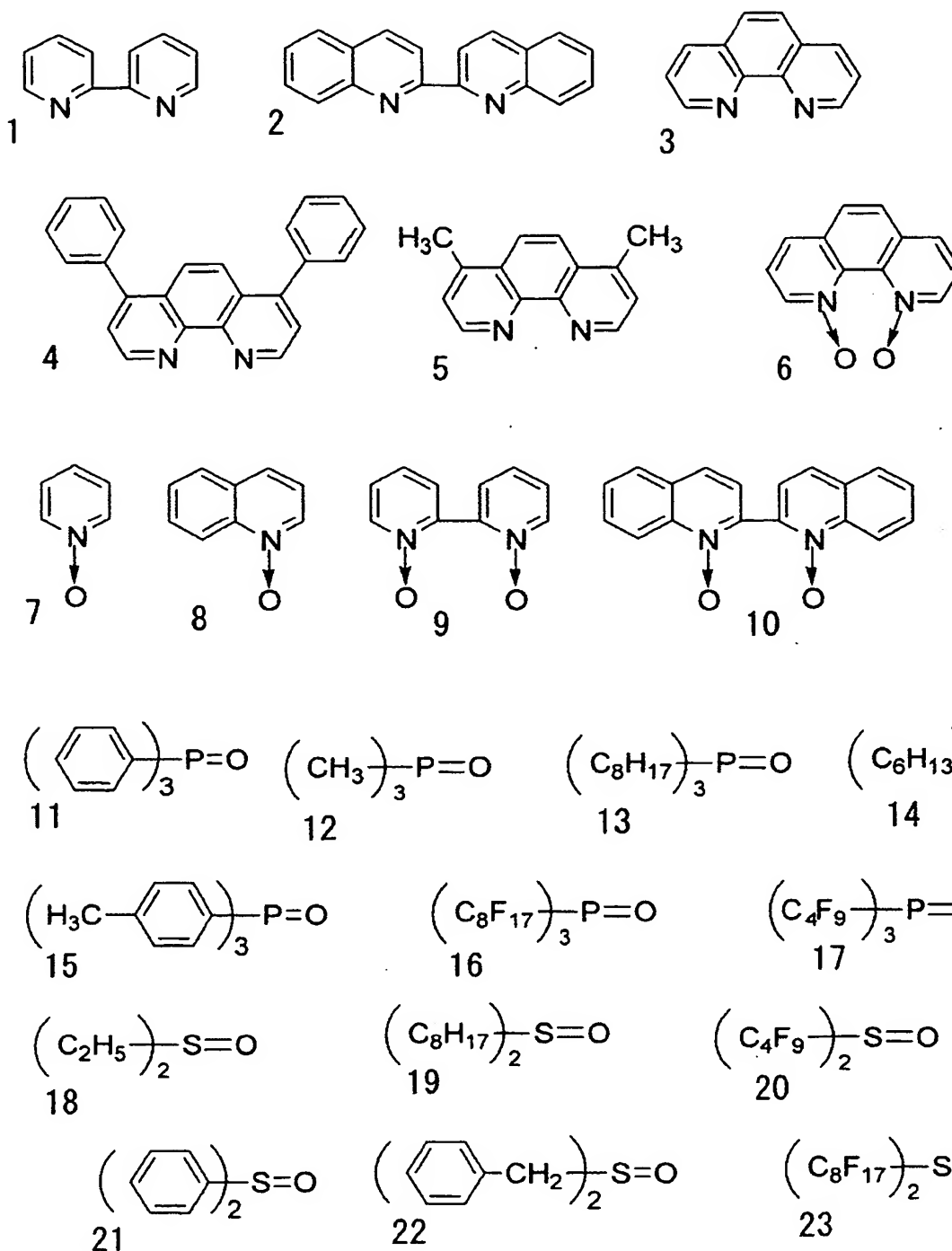
Also in these Lewis base compounds, like a bipyridine or a phenanthroline, when [, such as the atom configured in intramolecular, for example, a nitrogen atom etc.,] two pieces exist, the same work as two auxiliary ligands may be carried out with one Lewis base compound. In addition, the substituent mentioned above is illustrated as a substituent permuted by these Lewis base compounds. An alkyl group, an aryl group, an ARUKOSHIKIRU radical, an aralkyl radical, an aryloxy group, a halogen radical, etc. are desirable especially.

[0030]

The example (1-23) of the Lewis base compound (R2) used as an auxiliary ligand is illustrated below. In addition, the Lewis base compound used in the gestalt of this operation is not limited to these.

[0031]

[Formula 3]

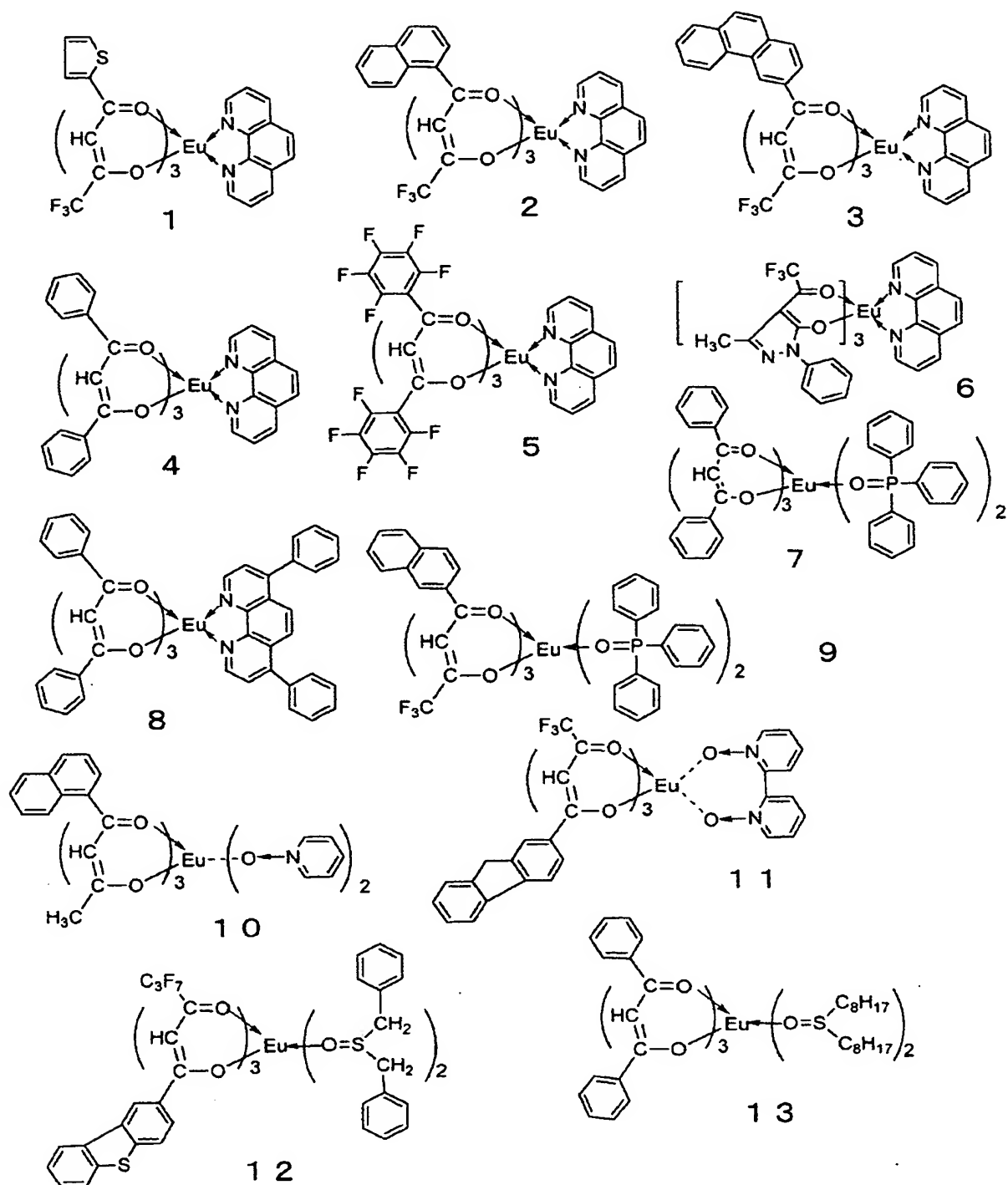


[0032]

The example (1-13) of an europium complex expressed with a general formula (2) is shown below. In addition, in the gestalt of this operation, it is not limited to these.

[0033]

[Formula 4]



[0034]

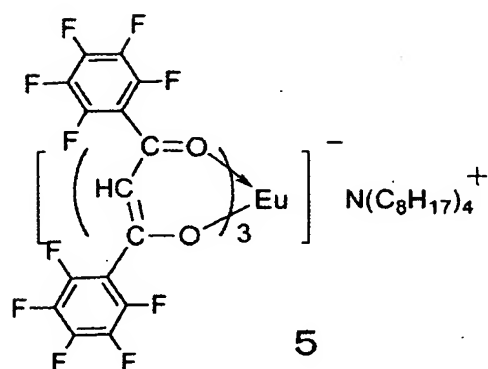
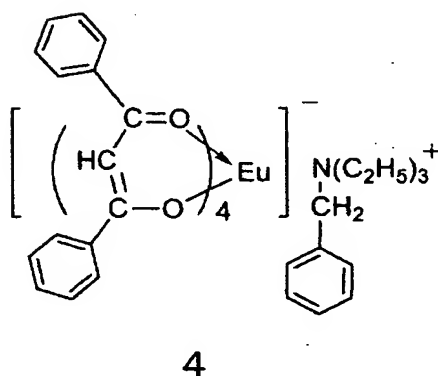
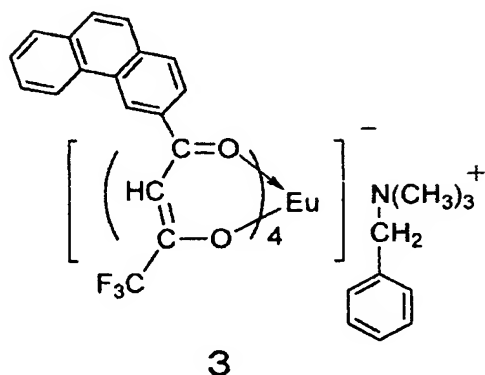
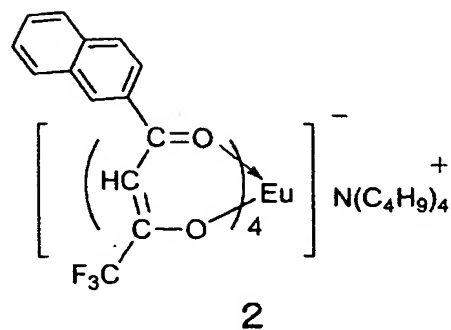
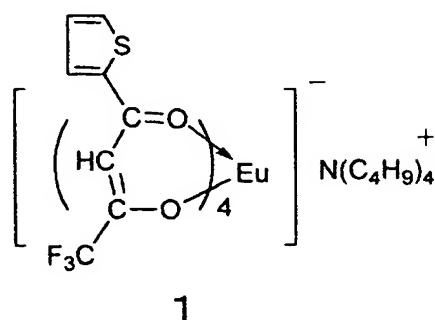
Next, the europium complex expressed with a general formula (3) is explained. As ammonium ion in a general formula (3), the quaternary ammonium salt guided from alkylamine, arylamine, and aralkyl ion is mentioned. As a substituent of an amine, arylated alkyl radicals, such as aryl group; benzyls, such as permutation alkyl group; phenyls, such as alkyl group; hydroxyethyl, such as methyl, ethyl, propyl, butyl, hexyl, and octyl, and methoxy ethyl, and tolyl, and a phenethyl radical, etc. are mentioned.

[0035]

The example (1-5) of an europium complex expressed with a general formula (3) is shown below. In addition, in the gestalt of this operation, it is not limited to these.

[0036]

[Formula 5]



[0037]

As a complex which makes a ligand the carboxylic-acid ion which is another compound of a rare earth ion complex, and which has a substituent containing an aromatic series radical, the europium complex expressed with the following general formula (4) is mentioned, for example.

$(R4-(X)_n-COO)_3Eu(R5)_2$ (4)

(R4 is a radical containing the aromatic hydrocarbon ring or at least one aromatic heterocycle which may have a substituent among a formula, X is a divalent connection radical, n is 0 or 1 and R5 is an auxiliary ligand which consists of a Lewis base.)

[0038]

As for the ligand expressed with a general formula (4), it is desirable from the point of an absorption wavelength region to use as a ligand the carboxylic-acid ion which has eight or more pi electrons and constitutes pi electron conjugated system including at least one aromatic series ring. Moreover, although the triplet energy of the parent compound of carboxylic-acid ion will not be restricted especially if it is higher than europium ion excitation state energy level, as for the number of an aromatic series ring, it is usually desirable to use the aromatic series or the aromatic heterocycle below 3 ring type. The triplet energy excited by absorbing the light from the semi-conductor light emitting device 11 becomes low, and compounds, such as a pyrene which has four or more rings of aromatic series rings when the number of an aromatic series ring is four or more rings, have a possibility that an europium complex may stop emitting light.

[0039]

As for R4 in a general formula (4), it is desirable that it is the univalent radical guided from the aromatic series ring or complex aromatic series ring below 3 ring type which may have a substituent. As an aromatic series ring, the compound

guided from aromatic hydrocarbon, such as aromatic series monocycle type hydrocarbons, such as benzene, naphthalene, an indene, biphenylene, an acenaphthene, a fluorene, a phenanthrene, a tetralin, an indan, and an indene, or an aromatic series condensed multi-ring type hydrocarbon; benzoquinone, a naphthoquinone, and anthraquinone, is mentioned, for example. As a complex aromatic series ring, aromatic series monocycle type heterocycles, such as a furan, a pyrrole, a thiophene, oxazole, isoxazole, a thiazole, an imidazole, a pyridine, benzofuran, benzothiophene, a coumarin, benzopyran, a carbazole, a xanthene, a quinoline, and triazine, or aromatic series condensed multi-ring type heterocycle is mentioned.

[0040]

moreover, as a substituent which R4 may have Alkyl groups, such as methyl, ethyl, propyl, and butyl; Trifluoromethyl, fluoro alkyl group [, such as pentafluoro ethyl,]; — cycloalkyl radical [, such as a cyclohexyl radical,]; — ethynyl group; — phenyl ethynyl — Aryl ethynyl groups, such as pyridyl ethynyl and thienyl ethynyl; Methoxy, The alkoxy group of ethoxy **: Aryl group; benzyls, such as phenyl and naphthyl, Aralkyl radicals, such as phenethyl; Phenoxy, naphthoxy one, the aryloxy group; hydroxyl; allyl group; acetyl of biphenyl oxy-**, Acyl groups, such as a propionyl, benzoyl, toluoyl, and biphenyl carbonyl; Acetoxy, Acyloxy radicals, such as propionyloxy and benzoxyloxy one; Methoxycarbonyl, alkoxy carbonyl group [, such as ethoxycarbonyl,]; — aryloxy carbonyl group [, such as phenoxy carbonyl]; — carboxyl group; — carbamoyl group; — amino-group; — dimethylamino — Permutation amino groups, such as diethylamino, methylbenzyl amino, diphenylamino, and acetyl methylamino; A methylthio, Permutation sulfonyl radical; cyano groups, such as permutation thio radical; sulfhydryl group; ethyl sulfonyls, such as ethyl thio, phenylthio, and benzyl thio, and a phenyl sulfonyl radical; halogen radicals, such as fluoro, chloro, BUROMO, and iodine, etc. are mentioned. Also in these, an alkyl group, an alkoxy group, an aryl group, a cycloalkyl radical, a cycloalkyl radical, an aryloxy group, an aralkyl radical, an ethynyl group, and a halogen radical are desirable. In addition, R4 is not limited to these substituents. Moreover, these substituents may have a substituent further.

[0041]

Next, the carboxylic-acid ion in a general formula (4) is divided when it has with the case (n= 0) where it does not have X which is a divalent connection radical (n= 1). Furthermore, X is divided into two kinds of gestalten when not having, when it has a carbonyl group when it has X which is a divalent connection radical (n= 1). For this reason, the carboxylic-acid ion in a general formula (4) is further expressed with the following general formula (5) which does not have a carbonyl group, and the general formula (6) which has a carbonyl group. any of the complex structure where an europium complex makes these carboxylic-acid ion a ligand — although — it can be used.

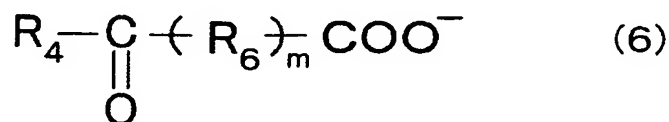
[0042]

[Formula 6]



[0043]

[Formula 7]



[0044]

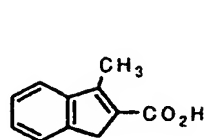
Among a general formula (5) and a general formula (6), be [what is necessary / just although R6 becomes a divalent connection radical], the divalent connection radical guided from an alkylene group, the divalent connection radical guided from a ring set hydrocarbon, an aliphatic series ring, an aromatic series ring, and heterocycle, for example is mentioned. Moreover, m is 0 or 1 among a general formula (6). Methylene, ethylene, etc. are mentioned as an alkylene group of R6. As a ring set hydrocarbon, a biphenyl, a terphenyl, binaphthyl, cyclohexylbenzene, phenyl naphthalene, etc. are mentioned. As an aliphatic series ring, a cyclopentane, a cyclohexane, cycloheptane, norbornane, bicyclo hexyl, etc. are mentioned. The compound same as an aromatic series ring as the example of an aromatic series ring mentioned above is mentioned. As heterocycle, aliphatic series heterocycles other than the aromatic heterocycle mentioned above, such as pyrazoline, a piperazine, imidazolidine, and a morpholine, are mentioned. In addition, oxy-alkylenes [, such as thio alkylene;-OCH2-], such as -SCH2-; vinylene (-C=C-) etc. is mentioned. In addition, R6 is not limited to these divalent substituents. Moreover, these divalent substituents may have a substituent further.

[0045]

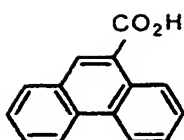
The example of a carboxylic acid in which the carboxylic-acid ion in a general formula (4) is guided is illustrated below. In addition, the carboxylic acid used in the gestalt of this operation is not limited to these. In a general formula (4), as for a compound in case n is 0, the following carboxylic acids (1-10) are mentioned.

[0046]

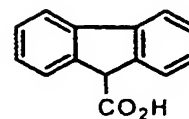
[Formula 8]



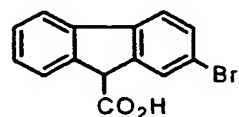
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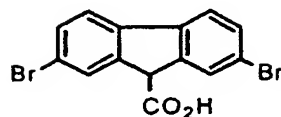
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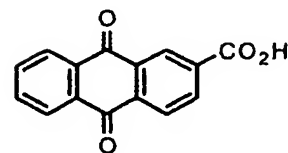
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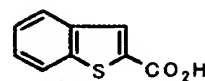
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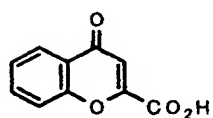
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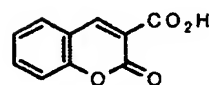
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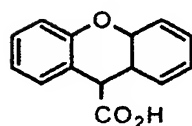
7



8



9



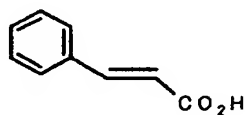
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[0047]

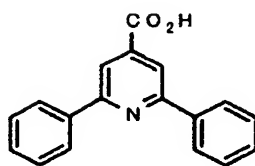
Next, in a general formula (4), n is 1, and, as for a compound in case X is R6 (general formula (5)), the following carboxylic acids (11-15) are mentioned.

[0048]

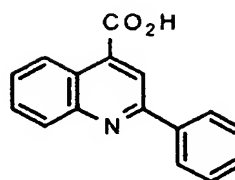
[Formula 9]



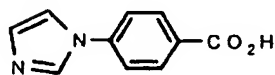
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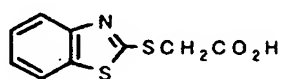
12



13



14



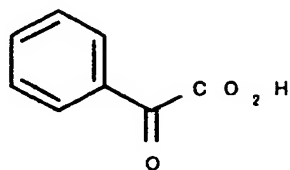
15

[0049]

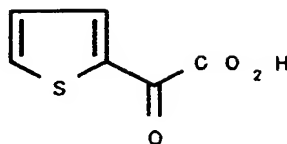
Next, in a general formula (6), as for a compound in case m is 0, the following carboxylic acids (16 and 17) are mentioned.

[0050]

[Formula 10]



16



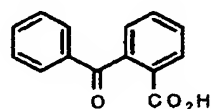
17

[0051]

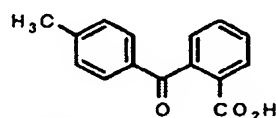
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenyl group and R6 is a phenyl group, the following carboxylic acids (18-30) are mentioned.

[0052]

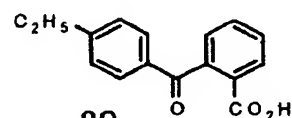
[Formula 11]



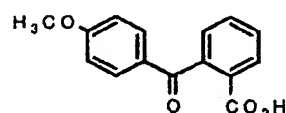
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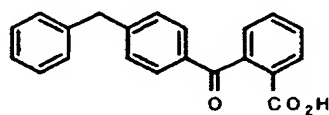
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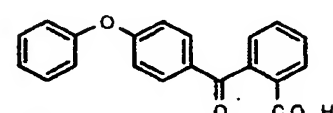
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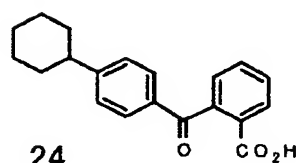
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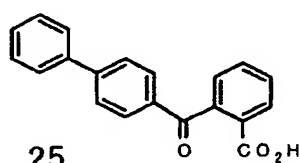
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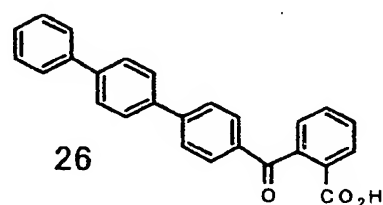
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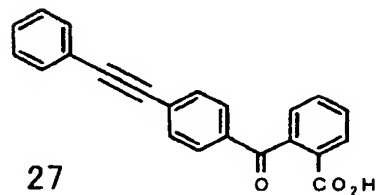
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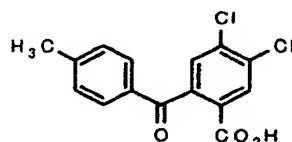
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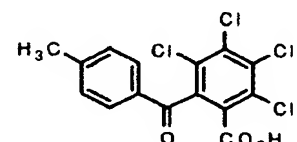
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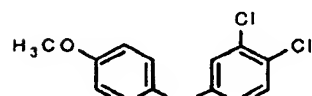
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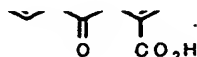
28



29



30

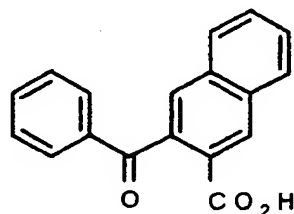


[0053]

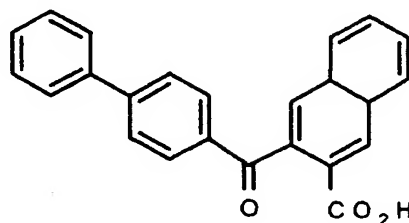
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenyl group and R6 is a naphthyl group, the following carboxylic acids (31-34) are mentioned.

[0054]

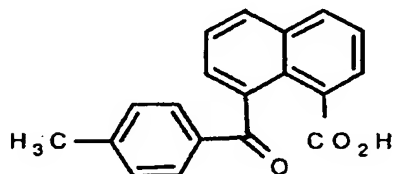
[Formula 12]



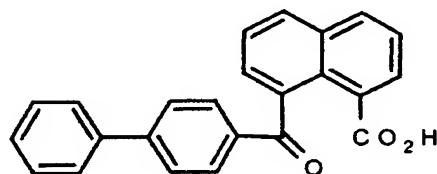
31



32



33



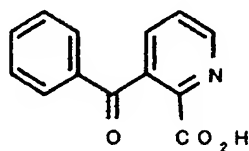
34

[0055]

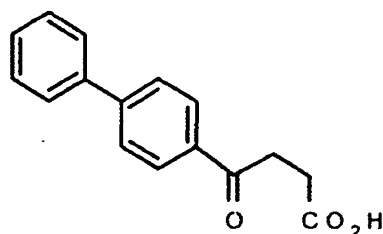
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenyl group and R6 is other radicals, the following carboxylic acids (35-37) are mentioned.

[0056]

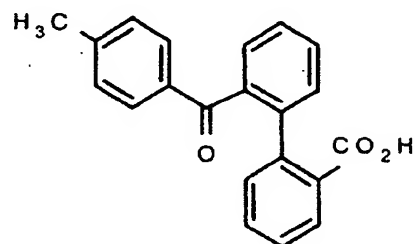
[Formula 13]



35



36



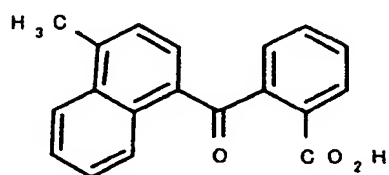
37

[0057]

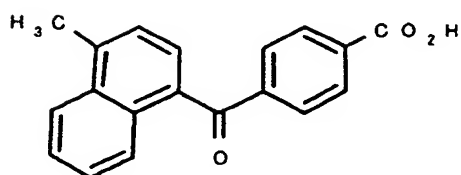
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a naphthyl group and R6 is an aromatic series ring, the following carboxylic acids (38-41) are mentioned.

[0058]

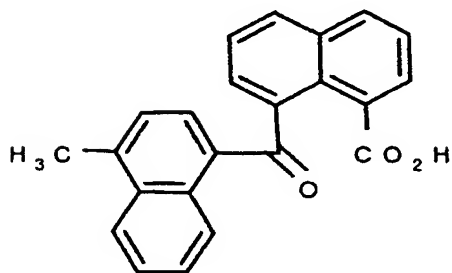
[Formula 14]



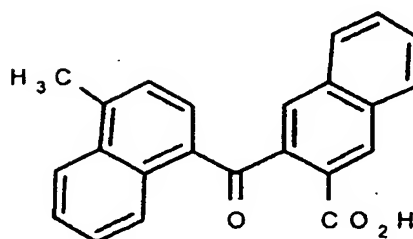
38



39



40



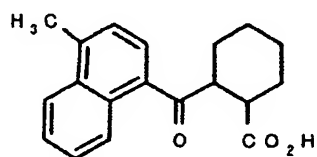
41

[0059]

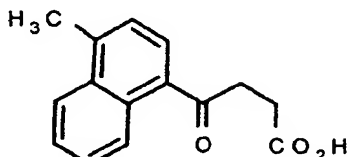
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a naphthyl group and R6 is other radicals, the following carboxylic acids (42-44) are mentioned.

[0060]

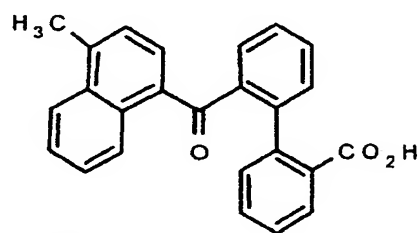
[Formula 15]



42



43



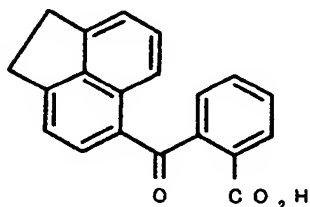
44

[0061]

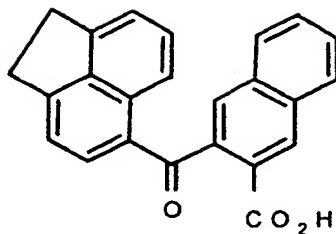
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is an acenaphtyl radical and R6 is a phenyl group and others, the following carboxylic acids (45-48) are mentioned.

[0062]

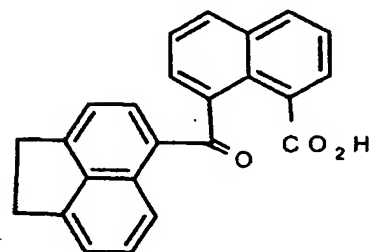
[Formula 16]



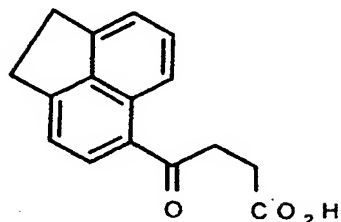
45



46



47



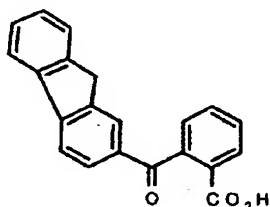
48

[0063]

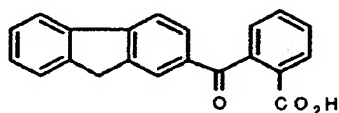
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a fluorenyl group and R6 is a phenyl group, the following carboxylic acids (49-55) are mentioned.

[0064]

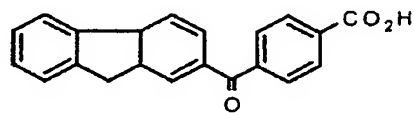
[Formula 17]



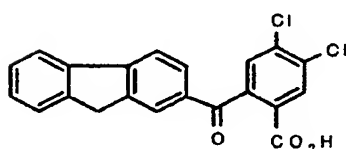
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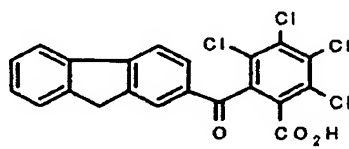
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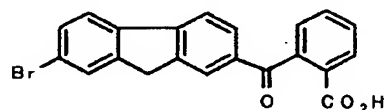
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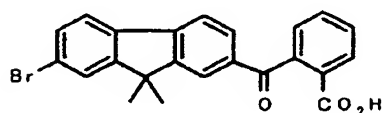
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53



54



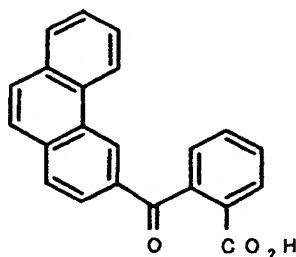
55

[0065]

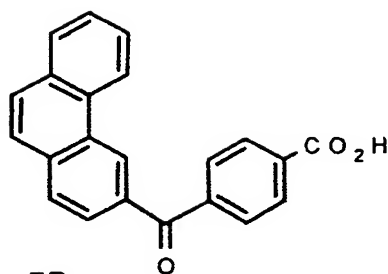
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenan TORENIRU radical and R6 is a phenyl group and others, the following carboxylic acids (56-59) are mentioned.

[0066]

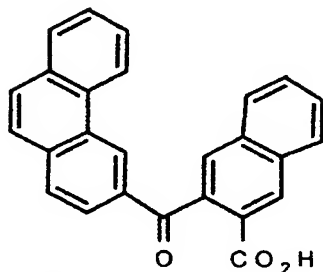
[Formula 18]



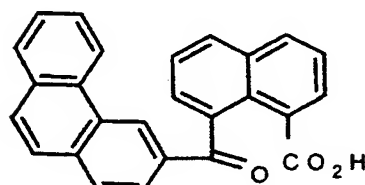
56



57



58



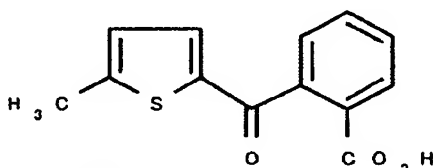
59

[0067]

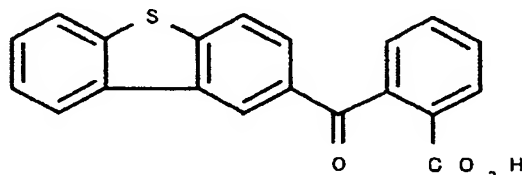
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a heterocycle radical and R6 is a phenyl group, the following carboxylic acids (60 and 61) are mentioned.

[0068]

[Formula 19]



60



61

[0069]

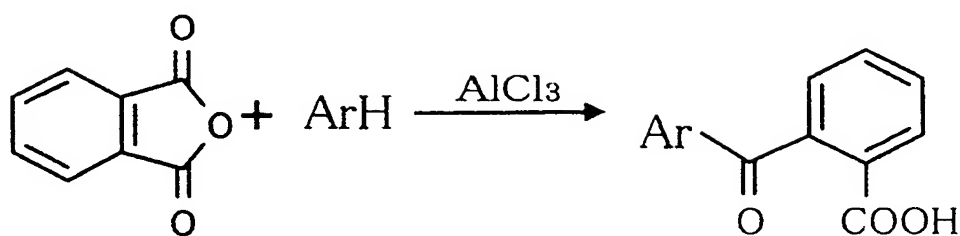
The carboxylic acid with which the carboxylic-acid ion as a ligand in a general formula (4) is guided is compoundable by the well-known synthetic approach. The synthesis method is indicated by the volume composition of an organic compound, 14th volume "reaction (II)" 921st page (1977) Chemical Society of Japan editing of a new experimental science lecture, or for 22nd volume "organic synthesis IV" 1st page (1992) Chemical Society of Japan of the 4th edition experimental science lecture etc., for example. As a typical synthesis method, oxidation reaction of a corresponding primary alcohol and a corresponding aldehyde, the hydrolysis reaction of ester or nitril, the Friedel Crafts reaction by the acid anhydride, etc. are mentioned.

[0070]

Especially, in the Friedel Crafts reaction using the cyclic anhydride of dicarboxylic acid, such as phthalic anhydride, naphthalic acid anhydride, anhydrous amber acid, diphenic acid anhydride, 1, 2-cyclohexane dicarboxylic acid anhydride, 2, and 3-pyridazine dicarboxylic acid anhydride, the carboxylic acid which has a carbonyl group in intramolecular is compoundable. For example, according to the Friedel Crafts reaction using aromatic hydrocarbon or an aromatic heterocycle, and phthalic anhydride, as shown in the following reaction formula, the carboxylic acid which the carbonyl group combined with the ortho position of the benzene ring can compound easily. The carboxylic acid which the carbonyl group combined with the ortho position of the benzene ring is desirable from a complex with high brightness being easy to be obtained compared with a para-position substitution product. In addition, Ar expresses aromatic hydrocarbon or an aromatic heterocycle among a formula.

[0071]

[Formula 20]



[0072]

The same compound as the auxiliary ligand (R2) which consists of a Lewis base in the general formula (2) mentioned above as an auxiliary ligand (R5) which consists of a Lewis base in a general formula (4) is mentioned.

[0073]

a fluorescent substance layer 12 accept for example, an europium complex and a need, and prepare other rare earth ion complexes, other organic fluorescent substances, and an inorganic fluorescent substance as a resin constituent which be made to dissolved or distribute in suitable binder resin, and be mixed, and this be arrange by the approach of spreading and others in the luminescence equipment 10 with which the gestalt of this operation be apply in the location which absorb the light from semi-conductor light emitting devices 11, such as a wall of an external cap 13. As binder resin, thermoplastics, thermosetting resin, a photo-setting resin, etc. are usually mentioned. Specifically, cellulose type resin; epoxy resin; phenol resin; silicone resin, such as styrene resin; polycarbonate resin; polyester resin; phenoxy resin; butyral resin; polyvinyl alcohol; ethyl cellulose, such as methacryl-resin; polystyrene, such as Pori methacrylic acid methyl, and a styrene acrylonitrile copolymer, cellulose acetate, and cellulose acetate butylate, etc. is mentioned.

[0074]

The luminescence equipment 10 with which the gestalt of this operation is applied can emit light in the white light by having with a blue fluorescent substance and a green fluorescent substance, and combining these further, with the red fluorescent substance containing rare earth ion complexes, such as an europium complex. In addition, the fluorescent substance containing other organic red fluorescent substances and an inorganic red fluorescent substance may also be included if needed. A well-known fluorescent substance can be used as a blue fluorescent substance or a green fluorescent substance. For example, as a blue fluorescent substance, inorganic fluorescent substances, such as ZnS:Ag, Sr5(PO4)3Cl:Eu, and BaMgAl10O17:Eu, are mentioned. moreover — as a green fluorescent substance — ZnS:Cu, ZnS:CuAl, and BaMgAl10O17: — inorganic fluorescent substances, such as Eu and Mn, are mentioned. Moreover, in addition to this, a thulium complex is mentioned as a blue fluorescent substance, and organic fluorescent substances, such as a terbium complex, are mentioned as a green fluorescent substance. The carboxylic-acid ion containing beta-diketone anion used for everything but a well-known ligand as a ligand of the europium complex in the gestalt of this operation as a ligand of these complexes or an aromatic series radical can be used.

[0075]

What is necessary is just to arrange the approach of applying the fluorescent substance resin layer containing the mixture of a red fluorescent substance, a blue fluorescent substance, and a green fluorescent substance inside the external cap 13, and forming the fluorescent substance layer 12, or this fluorescent substance resin layer on the semi-conductor light emitting device 11, in order to make the white light emit light. In this case, a red fluorescent substance does not necessarily need to be mixed with a blue fluorescent substance and a green fluorescent substance in the same resin, and the laminating of the resin layer which contains a red fluorescent substance on the resin layer containing a blue fluorescent substance and a green fluorescent substance may be carried out.

[0076]

Next, the gestalt of other operations of the luminescence equipment with which this invention is applied is explained. Drawing 2 is drawing for explaining the luminescence equipment in the gestalt of the 2nd operation. Here, the laminating of the resin layer containing an inorganic fluorescent substance and the fluorescent substance layer containing a complex is carried out one by one on the semi-conductor light emitting device. The external cap 23 the luminescence equipment 20 shown in drawing 2 was formed with a bonnet, glass, etc. in the upper part of a blanket 28 and a blanket 28, Mounting lead 26b and inner lead 26a which were attached in the blanket 28, Mounting lead 26b and inner lead 26a, and flowing electric contact 29, The semi-conductor light emitting device 21 contained in the cup of the mounting lead 26b upper part, The inorganic fluorescent substance layer 27 with which it filled up in the cup of the mounting lead 26b upper part, A rare earth ion complex etc. has the fluorescent substance layer 22 by which mixed distribution was carried out into binder resin, and conductive wire 25a and conductive wire 25b, and, as for the interior of the external cap 23, it fills up with inert gas 24, such as a vacuum or nitrogen gas, and argon gas.

[0077]

In addition, the endurance of a fluorescence complex can be further raised by easing the effect of the heat generated when a semi-conductor light emitting device emits light. For example, the approach of preparing a semi-conductor light emitting device and the fluorescent substance layer which contains a fluorescence complex for space through other layers, such as a partition or a thermal break, and an optical diffusion layer, the approach of carrying out the laminating of a heat-resistant inorganic high fluorescent substance layer and the fluorescent substance layer containing a fluorescence complex, etc. are mentioned. The heat deterioration of the fluorescent substance containing the complex which consists of an organic material which is generally inferior to thermal resistance by this compared with an inorganic fluorescent substance can be suppressed, and luminescence equipment excellent in endurance can be obtained.

[0078]

For example, it is desirable that the layer which consists of an inorganic fluorescent substance, and the layer of the fluorescent substance containing a complex are the layered products separated, respectively when a fluorescent substance approaches the semi-conductor light emitting device 21 and is arranged like the luminescence equipment 20 shown in drawing 2, and it is desirable that it is the layer of the direction with the inorganic fluorescent substance

layer near a light emitting device. That is, the heat generated by luminescence of the semi-conductor light emitting device 21 can ease heating the fluorescent substance layer 22 locally by arranging the inorganic fluorescent substance layer 27 which contains an inorganic fluorescent substance between the semi-conductor light emitting device 21 and the fluorescent substance layer 22 containing a complex. Moreover, in the case of the shell mold configuration which is the general gestalt of LED, a fluorescent substance is also mixable in closure resin, such as an epoxy resin. In this case, the light from a fluorescent substance turns into light diffused more.

[0079]

The luminescence equipment 10 and the luminescence equipment 20 with which the gestalt of this operation is applied are independent, or can be used as various lighting systems by combining plurality. As a lighting system, a lighting lamp, the back light for liquid crystal panels, super-thin lighting, etc. are mentioned, for example.

[0080]

[Example]

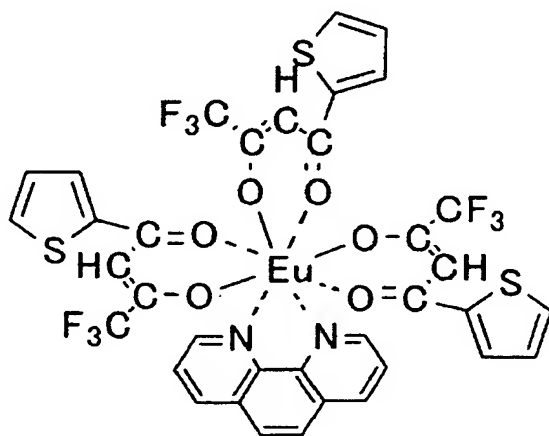
An example is given to below and the gestalt of this operation is explained more concretely. In addition, the gestalt of this operation is not limited to an example. Moreover, the section in an example and especially % are weight criteria altogether, unless it refuses.

(Examples 1-2, example of a comparison)

The europium (Eu) complex 10 section which makes a ligand beta-diketone shown by the following formula, and the methyl-ethyl-ketone solution (20% of concentration) 200 section of a polyvinyl butyral (Sekisui Chemical Co., Ltd. make S lek BL-1) were mixed, and the mixed solution was prepared, and these mixed solutions 0.2-0.3g were applied to the interior of glass ampul with a diameter of 14mm, it dried, and the coat of a fluorescent substance was formed. Next, this ampul was processed on the conditions ((1) vacuum lock (2.5x10 to 5 torrs), (2) nitrogen gas charging (20 ppm or less of oxygen densities), (3) air enclosure (about 20% of oxygen densities)) shown in a table 1, and the coat of the fluorescent substance containing Eu complex created the glass ampul applied to the inner surface. Next, the light from ultraviolet to a visible region was irradiated in this glass ampul for 40 hours using the fading-test machine (Ci4000 by the atlas company), respectively, and the fluorescence intensity of the fluorescent substance containing an europium (Eu) complex was measured after that using the Hitachi fluorescence spectrometry machine F4500. The fluorescence intensity of a fluorescent substance is expressed as a characteristic which set fluorescence intensity when not irradiating light by the fading-test machine to 100. Lightfastness is so good that a numeric value is close to 100. A result is shown in a table 1.

[0081]

[Formula 21]



[0082]

[A table 1]

	実 施 例		比較例
	1	2	
	真空	窒素ガス	空気
光照射時間 0	1 0 0	1 0 0	1 0 0
4 0 時間	9 0	8 2	0 . 3

[0083]

When irradiating light from the result of a table 1 at the fluorescent substance put on the vacua (example 1), and when irradiating light at the fluorescent substance put on the bottom of nitrogen-gas-atmosphere mind (example 2), the lightfastness of a fluorescent substance is good and each is understood that endurance improves. On the other hand, when light is irradiated at the fluorescent substance placed into air (example of a comparison), it falls to 30% 40 hours after, and it turns out that lightfastness is remarkably poor.

[0084]

[Effect of the Invention]

In this way, according to this invention, the endurance of the fluorescent substance containing a fluorescence complex is raised, and the luminescence equipment which can be made to generate luminescence of high intensity, and the lighting system which used it are offered.

[Brief Description of the Drawings]

[Drawing 1] It is drawing for explaining the luminescence equipment with which the gestalt of this operation is applied.

[Drawing 2] It is drawing for explaining the luminescence equipment of the gestalt of the 2nd operation.

[Description of Notations]

10 20 [— 14 An external cap, 24 / — Inert gas, 15a, 15b 25a, 25b / — A conductive wire, 16a, 26a / — An inner lead, 16b, 26b / — 18 A mounting lead, 28 / — 19 A blanket, 29 / — Electric contact, 27 / — Inorganic fluorescent substance layer] — 11 Luminescence equipment, 21 — 12 A semi-conductor light emitting device, 22 — 13 A fluorescent substance layer, 23

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]

This invention relates to the luminescence equipment with which the endurance of a fluorescent substance was improved, and the lighting system which used this in more detail about luminescence equipment and a lighting system.
[0002]

[Translation done.]

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PRIOR ART

[Description of the Prior Art]

Conventionally, the luminescence equipment which carried out color conversion of the light of a discharge lamp or a semi-conductor light emitting device with the fluorescent substance is used for lighting etc. These luminescence equipments mix blue, red, and green light, and many examination is made in order to make the light of various colors of white and others emit light with color rendering properties uniform and sufficient in the large color reproduction range. The luminescence equipment which used semi-conductor light emitting devices, such as light emitting diode (LED) and semiconductor laser (LD), especially has high luminous efficiency, there is also an advantage of the environmental cure side of not using mercury, and development of the luminescence equipment which combined LED, LD, and a fluorescent substance is performed briskly.

[0003]

the fluorescent lamp with which inorganic red fluorescent substances, such as Y₂O₃:Eu, are used especially for the luminescence equipment used combining LED, LD, and the organic red fluorescent substance containing the europium (Eu) complex which makes the anion of beta-diketone a ligand — comparing — the light of near-ultraviolet light to the light — efficient — absorbing — high — it is reported as equipment which can obtain brightness luminescence (for

- example, patent reference 1 and patent reference 2 reference).

[0004]

[Patent reference 1]

JP,10-12925,A

[Patent reference 2]

** table No. 509912 [2000 to] official report

[0005]

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EFFECT OF THE INVENTION

[Effect of the Invention]

In this way, according to this invention, the endurance of the fluorescent substance containing a fluorescence complex is raised, and the luminescence equipment which can be made to generate luminescence of high intensity, and the lighting system which used it are offered.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]

By the way, it is known that it will be easy to carry out photodegradation of the fluorescence complexes, such as a rare earth ion complex used for such an organic red fluorescent substance etc., and development of LED or LD is turned in the direction which emits light in the light of short wavelength more in recent years. Consequently, degradation of a fluorescent substance, a sealing agent, etc. with which a large light in energy was irradiated became remarkable, and, for this reason, the need for utilization of luminescence equipment that endurance is required has arisen.

[0006]

This invention is made that the problem which was thrown into relief when developing the luminescence equipment which uses such a fluorescence complex should be solved. Namely, the object of this invention raises substantially the endurance of the fluorescent substance containing fluorescence complexes, such as rare earth ion complexes including the europium complex which is excellent in a luminescence property, and aims at offering the luminescence equipment which can be made to generate luminescence of high intensity, and the lighting system which used it.

[0007]

[Translation done.]

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MEANS

[Means for Solving the Problem]

That luminescence equipment with high endurance should be offered, when this invention person etc. considered photodegradation of fluorescence complexes, such as an europium complex, under various conditions, he found out that the lightfastness of a fluorescence complex improved under the reduced pressure to which it became clear that oxygen participates in photodegradation and it lowered the oxygen density, or in inert gas, such as nitrogen gas and an argon. That is, the luminescence equipment with which this invention is applied is equipped with the light emitting device which emits light in the light from near-ultraviolet light to a light field, and the fluorescent substance containing at least one sort of fluorescence complexes which emit light by the light from this light emitting device, and is characterized by putting the fluorescent substance on the bottom of a hypoxia concentration ambient atmosphere.

[0008]

the luminescence equipment which uses an inorganic red fluorescent substance by combining this light emitting device and a fluorescence complex with the range of 360 to 470nm using the semi-conductor light emitting device which emits light in the light which has peak wavelength as a light emitting device used for the luminescence equipment with which this invention is applied — comparing — high — brightness luminescence can be obtained. Moreover, the light of the light is [installing the fluorescent substance containing a fluorescence complex in the interior of the container formed with the light transmission nature ingredient] efficiently absorbable from the description, then near-ultraviolet light.

[0009]

Furthermore, the lightfastness of the fluorescent substance used for the luminescence equipment with which this invention is applied of the description, then the fluorescence complex contained in a fluorescent substance improves notably that the oxygen density is put on the bottom of an ambient atmosphere 100 ppm or less. Moreover, in order for the oxygen density on which a fluorescent substance is put to consider as the bottom of an ambient atmosphere 100 ppm or less, it is desirable that it is under a vacuum or the ambient atmosphere of inert gas.

[0010]

Moreover, as for the fluorescence complex contained in the fluorescent substance used for the luminescence equipment with which this invention is applied, it is desirable to be chosen out of a rare earth ion complex. As for especially the fluorescent substance used for the luminescence equipment with which this invention is applied, it is desirable that it is characterized by containing the fluorescence complex chosen from the rare earth ion complex which makes a ligand the anion guided from the carboxylic acid which has a substituent containing beta-diketone or the aromatic series ring which has a substituent containing an aromatic series ring. Moreover, as for a rare earth ion complex, it is desirable from the point of the improvement in brightness to make a Lewis base into an auxiliary ligand. Especially, as for a rare earth ion complex, it is desirable that it is an europium complex.

[0011]

It is desirable that it is the resin constituent which was made to dissolve or distribute a fluorescence complex and was mixed as a mode of this fluorescent substance. Moreover, the luminescence equipment with which this invention is applied can use as the description, then white luminescence equipment to have further the blue fluorescent substance and green fluorescent substance which emit light by the light from a light emitting device with the fluorescent substance which emits light in red by the light from light emitting devices, such as an europium complex.

[0012]

The container with which the luminescence equipment with which this invention is applied was formed the light transmission nature ingredient on the other hand, and the interior was maintained at the hypoxia concentration ambient atmosphere. If characterized by having the fluorescent substance in which it was prepared in the interior of this container, and the light emitting device which emits light in the light from near-ultraviolet light to a light field, a light emitting device, and space were established inside the container through a partition or other layers It can excel in endurance and can grasp as luminescence equipment of one apparatus which can generate luminescence of high intensity.

[0013]

In this case, as for a fluorescent substance, it is desirable to be prepared in the interior of the container maintained at the hypoxia concentration ambient atmosphere through the light emitting device and the optical diffusion layer. Moreover, a fluorescent substance may mix an inorganic fluorescent substance and the fluorescent substance containing a fluorescence complex, when using it with an inorganic fluorescent substance. Furthermore, when a fluorescent substance approaches a semi-conductor light emitting device and is arranged, it is desirable that the layer which consists of an inorganic fluorescent substance, and the layer which consists of a fluorescent substance containing a fluorescence complex are the layered products separated, respectively.

[0014]

And a lighting system equipped with the luminescence equipment with which this invention is applied can be offered.

[0015]

[Embodiment of the Invention]

The luminescence equipment with which the gestalt of this operation is applied is equipped with the light emitting device which emits light in the light from near-ultraviolet light to a light field, and the fluorescent substance containing at least one sort of fluorescence complexes which emit light by the light from this light emitting device, and the fluorescent substance is put on the bottom of a hypoxia concentration ambient atmosphere. The endurance of the bottom of a hypoxia concentration ambient atmosphere of a fluorescence complex improves here by being a thing

under the ambient atmosphere where an oxygen density is low, and putting a fluorescent substance on the bottom of such an ambient atmosphere from air. Although it becomes the bottom of a hypoxia concentration ambient atmosphere making it reduced pressure or a vacuum or by considering as the bottom of the ambient atmosphere of inert gas, in order to raise the lightfastness of a fluorescence complex more, it is desirable that an oxygen density is 1000 ppm or less.

Next, the luminescence equipment with which the gestalt of this operation is applied is explained. Drawing 1 is drawing for explaining the luminescence equipment in the gestalt of this operation. The external cap 13 with which the luminescence equipment 10 shown in drawing 1 was formed in the dome mold light transmission nature ingredients, such as a bonnet, for example, glass etc., in the upper part of a blanket 18 and a blanket 18, Mounting lead 16b and inner lead 16a which were attached in the blanket 18, Electric contact 19 which is attached in the lower part of a blanket 18 and flows with mounting lead 16b and inner lead 16a, The semi-conductor light emitting device 11 contained in the cup of the mounting lead 16b upper part, The fluorescent substance layer 12 of the coat which it filled up in the cup of the mounting lead 16b upper part, and mixed distribution of the red fluorescent substance was carried out into binder resin, and was applied inside the external cap 13, Conductive wire 15a which flows through inner lead 16a and the semi-conductor light emitting device 11, It has conductive wire 15b which flows through the semi-conductor light emitting device 11 and mounting lead 16b, and, as for the interior of the external cap 13, fills up with inert gas 14, such as a vacuum or nitrogen gas, and argon gas.

[0016]

The semi-conductor light emitting device 11 emits light in the light from near-ultraviolet light to a light field, and the fluorescent substance contained in the fluorescent substance layer 12 absorbs this light, and it emits light in the light of long wavelength more. Instead of filling up the interior of the external cap 13 with nitrogen gas, it is also possible by maintaining at a vacua to raise the lightfastness of the fluorescent substance layer 12 and to raise the endurance of luminescence equipment 10. Although the relation between the oxygen density in the interior of the external cap 13 and the degradation behavior of the fluorescence complex contained in the fluorescent substance layer 12 containing a fluorescence complex is not clear, if light is preferably irradiated from the semi-conductor light emitting device 11 under an ambient atmosphere 20 ppm or less, lightfastness will improve a fluorescence complex remarkably 100 ppm or less of oxygen densities. Moreover, lightfastness improves under low humidity.

[0017]

As a semi-conductor light emitting device 11, the laser diode (LD) or light emitting diode (LED) which has the peak wavelength of an emission spectrum in the range of 360 to 470nm is used. Especially as such a laser diode (LD) or light emitting diode (LED), although not limited, LD and LED which have peak wavelength from 380nm to 470nm, for example are desirable. Since organic compounds, such as a complex and resin, tend to carry out [tend] photodegradation of the semi-conductor light emitting device which has peak wavelength in a short wavelength side too much, it is not desirable. Moreover, when peak wavelength is in a long wavelength side too much, since the triplet energy level of the ligand of an europium complex becomes low and the width of face of selection of the ligand which can emit light becomes narrow, it is not desirable.

[0018]

The fluorescent substance layer 12 is formed with the gestalt of the coat formed of spreading inside the external cap 13 in the resin constituent which consists of a fluorescence complex and resin. Especially as a fluorescence complex, although not limited, the rare earth ion complex which is a complex of one sort or two sorts or more of ligand anions and the ion of trivalent rare earth elements is usually used. Sm, Eu, Tb, Dy, Tm, etc. are mentioned as rare earth elements. Especially, as a red fluorescent substance, as Eu (europium) element and a blue fluorescent substance, the ion complex of Tb (terbium) element is found, and is used as Tm (thulium) element and a green fluorescent substance. In addition, in the fluorescent substance layer 12, it is also possible to use together suitably the organic fluorescent substance of others besides a rare earth ion complex and an inorganic fluorescent substance.

[0019]

An europium complex is desirable as a red fluorescent substance which emits light in high brightness in a difficult near-ultraviolet light exposure especially also in a rare earth ion complex with an inorganic fluorescent substance. Moreover, as for a rare earth ion complex, it is desirable that it is the complex which makes a ligand the carboxylic-acid ion which has a substituent containing the anion or aromatic series radical of beta-diketone which has a substituent containing an aromatic series ring. Hereafter, although an europium complex is mentioned as an example and explained as a rare earth ion complex, it is not restricted to this.

[0020]

As a complex which makes a ligand the anion of beta-diketone which has a substituent containing an aromatic series ring, the europium complex expressed with any one formula of the following general formula (1), (2), and the (3) is mentioned, for example.

(R1)3Eu (1)

(R1)3Eu(R2)2 (2)

[(R1) 4Eu] -R3+ (3)

(R1 is the anion of beta-diketone which has a substituent containing an aromatic series ring among a formula (1), (2), and (3), R2 is an auxiliary ligand which consists of a Lewis base, and + is the R3 4th class ammonium ion.)

[0021]

As beta-diketone which has a substituent containing the aromatic series ring in a formula (1), (2), and (3) If the substituent and beta-diketone containing an aromatic series ring are included in the structure, the connection approach Although it may be direct or you may connect by the divalent radical, what the direct aromatic series ring has connected with one [at least] ketone is desirable. It is desirable to have at least one aromatic series radical, and the aromatic hydrocarbon compound or aromatic heterocycle compound which may have a substituent is further mentioned as this aromatic series radical. As an aromatic hydrocarbon compound, benzene, naphthalene, a phenanthrene, a fluorene, etc. are mentioned, for example. As an aromatic heterocycle compound, the heterocyclic compound containing oxygen, such as a furan, a thiophene, pyrazoline, a pyridine, benzothiophene, a carbazole, a dibenzofuran, and a dibenzo thiophene, nitrogen, and a sulfur atom is mentioned.

[0022]

moreover, as a substituent of these aromatic hydrocarbon compounds or an aromatic heterocycle compound For example, alkyl groups, such as methyl, ethyl, propyl, and butyl; Trifluoromethyl, Fluoro alkyl groups, such as pentafluoro

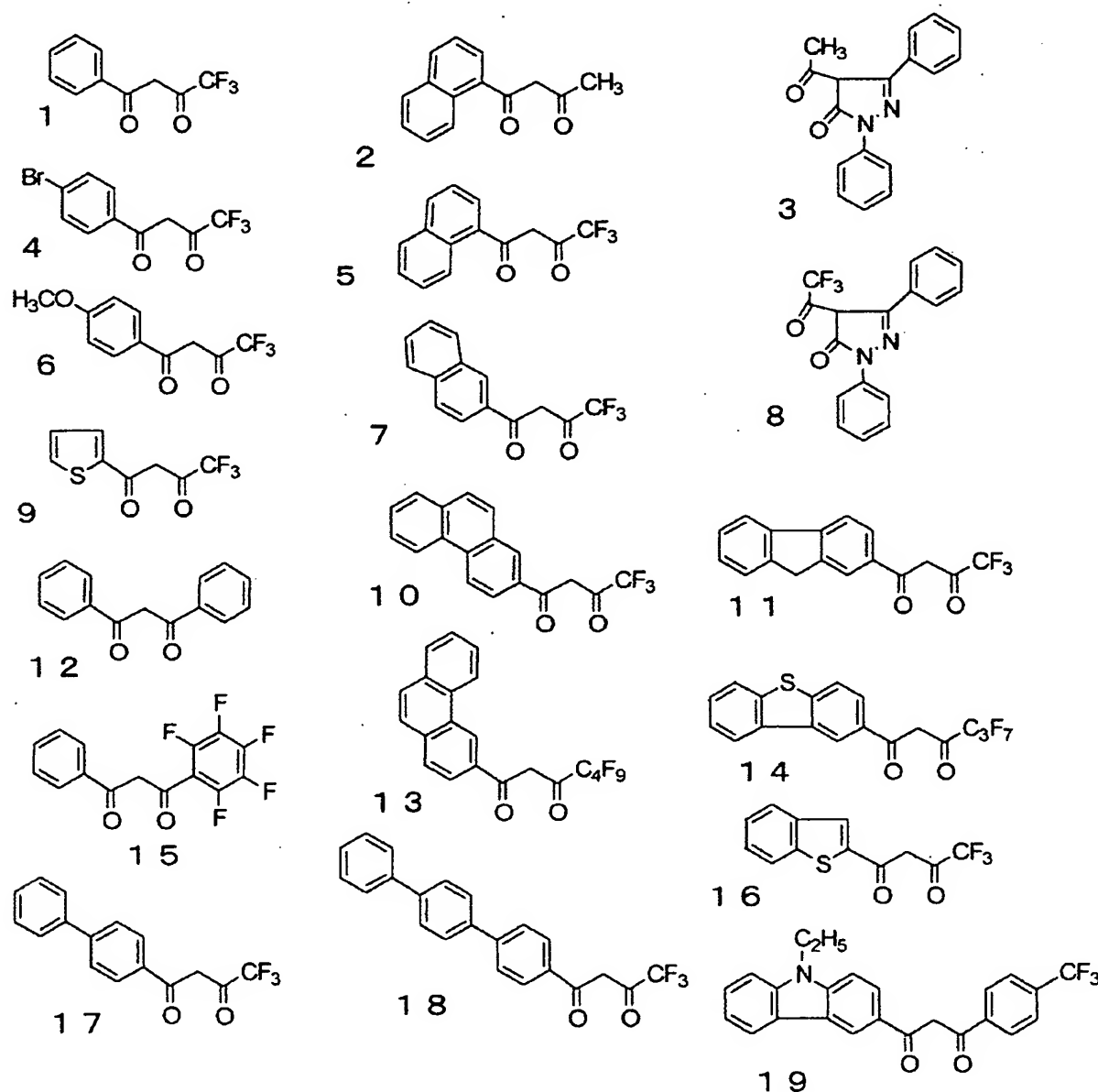
ethyl; Methoxy, the alkoxy group; phenyl of ethoxy **, Aryl groups, such as a naphthyl group; Aryloxy group; hydroxyl; allyl group; acetyls, such as benzyl and phenethyl, Acyl groups, such as a propionyl; Acyloxy radical; methoxycarbonyls, such as acetoxy, propionyloxy, and benzyloxy one, alkoxy carbonyl group [, such as ethoxycarbonyl,]; — aryloxy carbonyl group [, such as phenoxy carbonyl]; — carboxyl group; — carbamoyl group; — amino-group; — dimethylamino — Permutation amino groups, such as diethylamino, methylbenzyl amino, diphenylamino, and acetyl methylamino; A methylthio, Permutation sulfonyl radical; cyano groups, such as permutation thio radical; sulfhydryl group; ethyl sulfonyls, such as ethyl thio, phenylthio, and benzyl thio, and phenyl sulfonyl; halogen radicals, such as fluoro, chloro, BUROMO, and iodine, etc. are mentioned. It may join together mutually and these substituents may form a ring.

[0023]

As substituents other than the aromatic series radical which constitutes beta-diketone, the substituent of the aromatic hydrocarbon compound mentioned above or an aromatic heterocycle compound and the same substituent (however, a halogen radical is removed) are mentioned. The example (1-19) of beta-diketone which has a substituent containing an aromatic series ring is shown below. In addition, in the gestalt of this operation, it is not limited to these.

[0024]

[Formula 1]

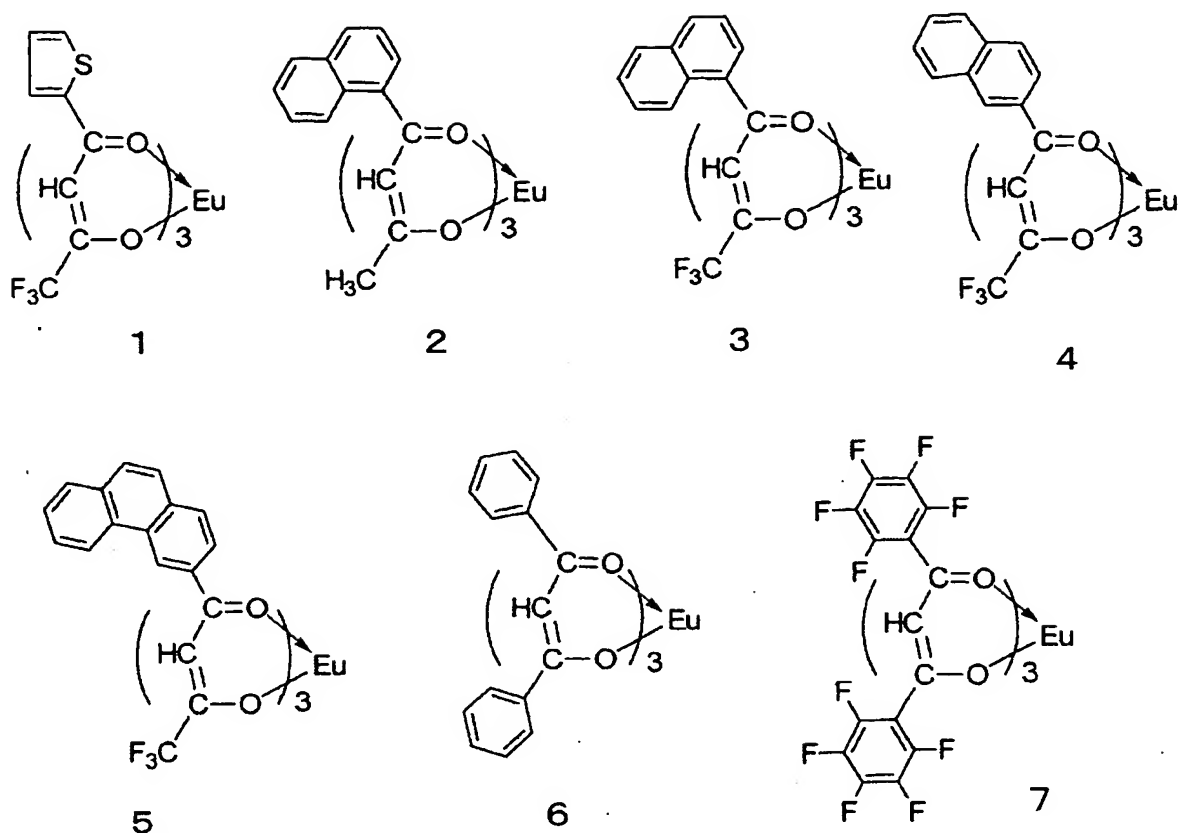


[0025]

The example (1-7) of an europium complex expressed with a general formula (1) is shown below. In addition, in the gestalt of this operation, it is not limited to these.

[0026]

[Formula 2]



[0027]

Next, the europium complex expressed with a general formula (2) is explained. It is chosen from the Lewis base compound which usually has the nitrogen atom or oxygen atom which can be configured to europium ion although not limited especially as an auxiliary ligand (R2) which consists of a Lewis base in a general formula (2). As those examples, the amine which may have a substituent, an amine oxide, phosphine oxide, a sulfoxide, etc. are mentioned. A compound different, respectively is sufficient as two Lewis base compounds used as an auxiliary ligand, and they may form one compound with two compounds.

[0028]

Specifically as an amine, a pyridine, pyrazine, quinoline, isoquinoline, phenanthridine, 2, and 2'-bipyridine, 1, 10-phenanthroline, etc. are mentioned. As an amine oxide, N-oxide of the above-mentioned amines, such as pyridine N-oxide, 2, 2'-bipyridine-N, and N'-dioxide, is mentioned. As phosphine oxide, triphenylphosphine oxide, trimethyl phosphine oxide, trioctyl phosphine oxide, etc. are mentioned. A diphenyl sulfoxide, a dioctyl sulfoxide, etc. are mentioned as a sulfoxide. The substituent mentioned above is illustrated as a substituent permuted by these. An alkyl group, an aryl group, an ARUKOSHIKIRU radical, an aralkyl radical, an aryloxy group, a halogen radical, etc. are desirable especially.

[0029]

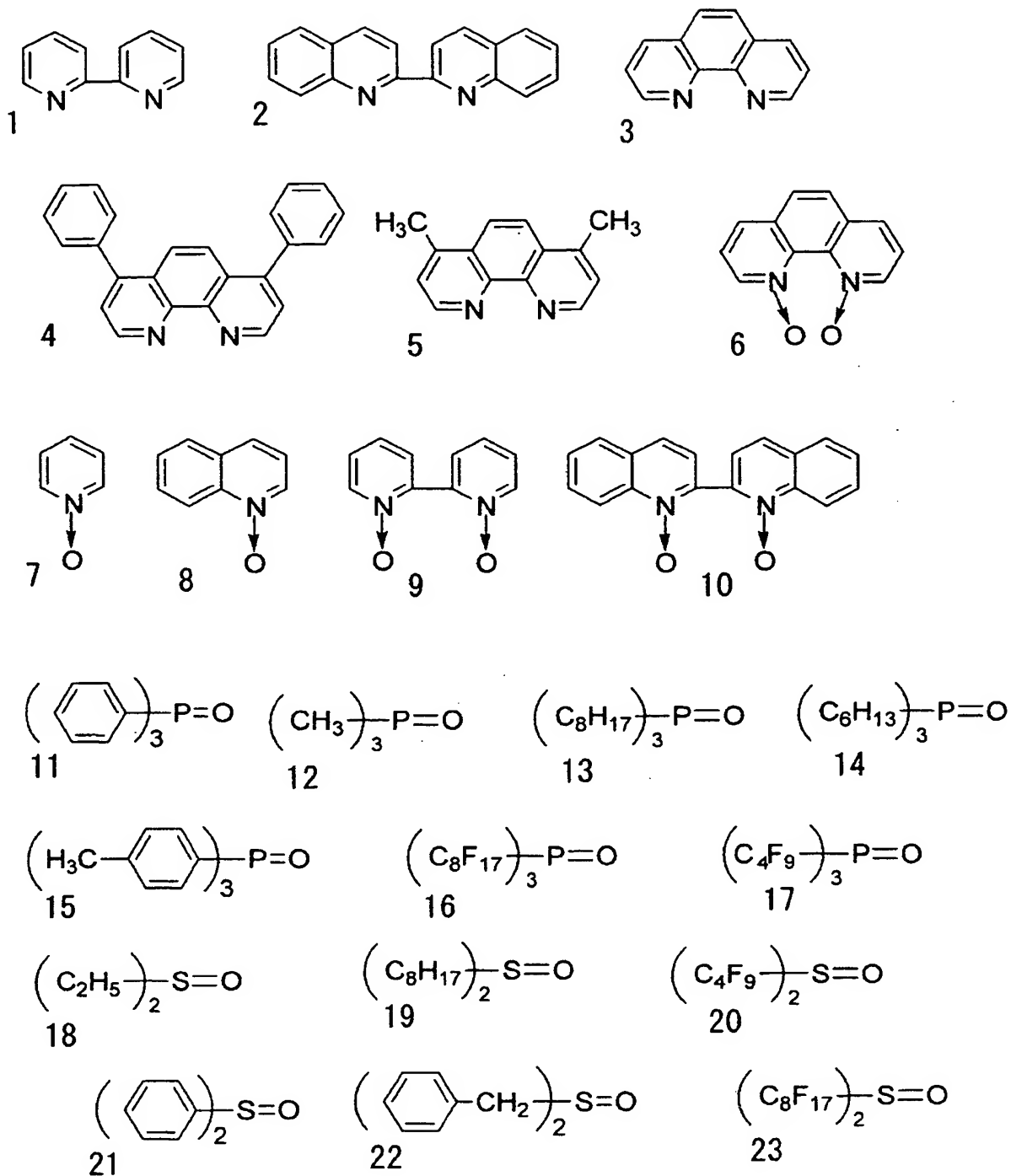
Also in these Lewis base compounds, like a bipyridine or a phenanthroline, when [, such as the atom configured in intramolecular, for example, a nitrogen atom etc.,] two pieces exist, the same work as two auxiliary ligands may be carried out with one Lewis base compound. In addition, the substituent mentioned above is illustrated as a substituent permuted by these Lewis base compounds. An alkyl group, an aryl group, an ARUKOSHIKIRU radical, an aralkyl radical, an aryloxy group, a halogen radical, etc. are desirable especially.

[0030]

The example (1-23) of the Lewis base compound (R2) used as an auxiliary ligand is illustrated below. In addition, the Lewis base compound used in the gestalt of this operation is not limited to these.

[0031]

[Formula 3]

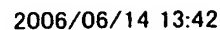


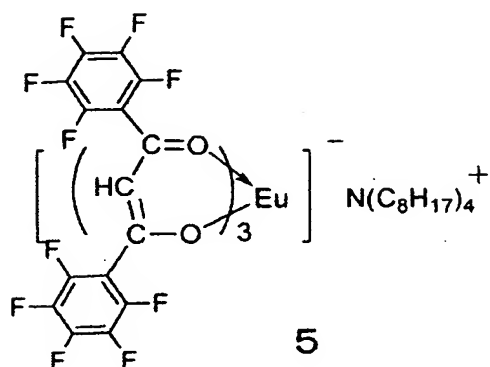
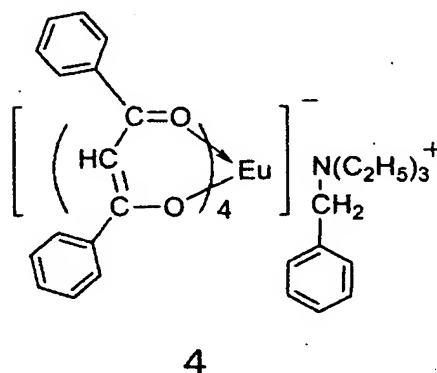
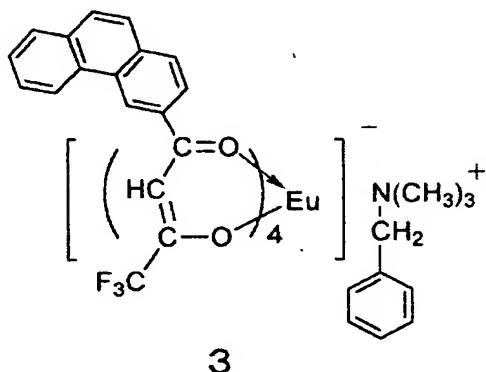
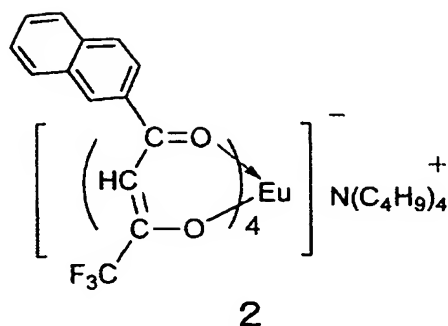
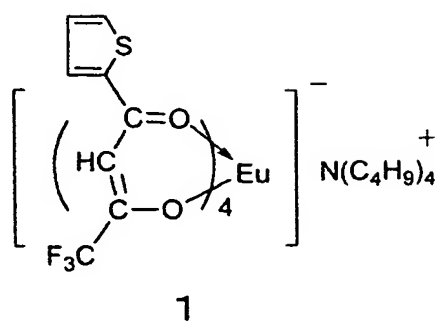
[0032]

The example (1-13) of an europium complex expressed with a general formula (2) is shown below. In addition, in the gestalt of this operation, it is not limited to these.

[0033]

[Formula 4]





[0037]

As a complex which makes a ligand the carboxylic-acid ion which is another compound of a rare earth ion complex, and which has a substituent containing an aromatic series radical, the europium complex expressed with the following general formula (4) is mentioned, for example.

$(R_4-(X)_n-COO)_3Eu(R_5)_2$ (4)

(R₄ is a radical containing the aromatic hydrocarbon ring or at least one aromatic heterocycle which may have a substituent among a formula, X is a divalent connection radical, n is 0 or 1 and R₅ is an auxiliary ligand which consists of a Lewis base.)

[0038]

As for the ligand expressed with a general formula (4), it is desirable from the point of an absorption wavelength region to use as a ligand the carboxylic-acid ion which has eight or more pi electrons and constitutes pi electron conjugated system including at least one aromatic series ring. Moreover, although the triplet energy of the parent compound of carboxylic-acid ion will not be restricted especially if it is higher than europium ion excitation state energy level, as for the number of an aromatic series ring, it is usually desirable to use the aromatic series or the aromatic heterocycle below 3 ring type. The triplet energy excited by absorbing the light from the semi-conductor light emitting device 11 becomes low, and compounds, such as a pyrene which has four or more rings of aromatic series rings when the number of an aromatic series ring is four or more rings, have a possibility that an europium complex may stop emitting light.

[0039]

As for R₄ in a general formula (4), it is desirable that it is the univalent radical guided from the aromatic series ring or complex aromatic series ring below 3 ring type which may have a substituent. As an aromatic series ring, the compound

guided from aromatic hydrocarbon, such as aromatic series monocycle type hydrocarbons, such as benzene, naphthalene, an indene, biphenylene, an acenaphthene, a fluorene, a phenanthrene, a tetralin, an indan, and an indene, or an aromatic series condensed multi-ring type hydrocarbon; benzoquinone, a naphthoquinone, and anthraquinone, is mentioned, for example. As a complex aromatic series ring, aromatic series monocycle type heterocycles, such as a furan, a pyrrole, a thiophene, oxazole, isoxazole, a thiazole, an imidazole, a pyridine, benzofuran, benzothiophene, a coumarin, benzopyran, a carbazole, a xanthene, a quinoline, and triazine, or aromatic series condensed multi-ring type heterocycle is mentioned.

[0040]

moreover, as a substituent which R4 may have Alkyl groups, such as methyl, ethyl, propyl, and butyl; Trifluoromethyl, fluoro alkyl group [, such as pentafluoro ethyl,]; — cycloalkyl radical [, such as a cyclohexyl radical,]; — ethynyl group; — phenyl ethynyl — Aryl ethynyl groups, such as pyridyl ethynyl and thienyl ethynyl; Methoxy, The alkoxy group of ethoxy **, Aryl group; benzyls, such as phenyl and naphthyl, Aralkyl radicals, such as phenethyl; Phenoxy, naphthoxy one, the aryloxy group; hydroxyl; allyl group; acetyl of biphenyl oxy-**, Acyl groups, such as a propionyl, benzoyl, toluoyl, and biphenyl carbonyl; Acetoxy, Acyloxy radicals, such as propionyloxy and benzoyloxy one; Methoxycarbonyl, alkoxy carbonyl group [, such as ethoxycarbonyl,]; — aryloxy carbonyl group [, such as phenoxy carbonyl]; — carboxyl group; — carbamoyl group; — amino-group; — dimethylamino — Permutation amino groups, such as diethylamino, methylbenzyl amino, diphenylamino, and acetyl methylamino; A methylthio, Permutation sulfonyl radical; cyano groups, such as permutation thio radical; sulfhydryl group; ethyl sulfonyls, such as ethyl thio, phenylthio, and benzyl thio, and a phenyl sulfonyl radical; halogen radicals, such as fluoro, chloro, BUROMO, and iodine, etc. are mentioned. Also in these, an alkyl group, an alkoxy group, an aryl group, a cycloalkyl radical, a cycloalkyl radical, an aryloxy group, an aralkyl radical, an ethynyl group, and a halogen radical are desirable. In addition, R4 is not limited to these substituents. Moreover, these substituents may have a substituent further.

[0041]

Next, the carboxylic-acid ion in a general formula (4) is divided when it has with the case (n= 0) where it does not have X which is a divalent connection radical (n= 1). Furthermore, X is divided into two kinds of gestalten when not having, when it has a carbonyl group when it has X which is a divalent connection radical (n= 1). For this reason, the carboxylic-acid ion in a general formula (4) is further expressed with the following general formula (5) which does not have a carbonyl group, and the general formula (6) which has a carbonyl group. any of the complex structure where an europium complex makes these carboxylic-acid ion a ligand — although — it can be used.

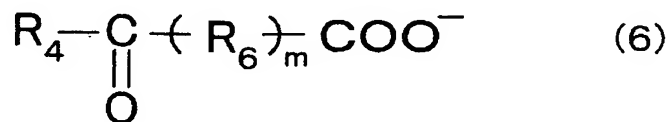
[0042]

[Formula 6]



[0043]

[Formula 7]



[0044]

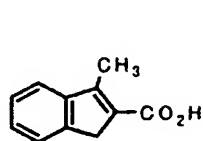
Among a general formula (5) and a general formula (6), be [what is necessary / just although R6 becomes a divalent connection radical], the divalent connection radical guided from an alkylene group, the divalent connection radical guided from a ring set hydrocarbon, an aliphatic series ring, an aromatic series ring, and heterocycle, for example is mentioned. Moreover, m is 0 or 1 among a general formula (6). Methylene, ethylene, etc. are mentioned as an alkylene group of R6. As a ring set hydrocarbon, a biphenyl, a terphenyl, binaphthyl, cyclohexylbenzene, phenyl naphthalene, etc. are mentioned. As an aliphatic series ring, a cyclopentane, a cyclohexane, cycloheptane, norbornane, bicyclo hexyl, etc. are mentioned. The compound same as an aromatic series ring as the example of an aromatic series ring mentioned above is mentioned. As heterocycle, aliphatic series heterocycles other than the aromatic heterocycle mentioned above, such as pyrazoline, a piperazine, imidazolidine, and a morpholine, are mentioned. In addition, oxy-alkylenes [, such as thio alkylene;-OCH2-], such as -SCH2-; vinylene (-C=C-) etc. is mentioned. In addition, R6 is not limited to these divalent substituents. Moreover, these divalent substituents may have a substituent further.

[0045]

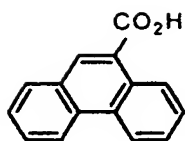
The example of a carboxylic acid in which the carboxylic-acid ion in a general formula (4) is guided is illustrated below. In addition, the carboxylic acid used in the gestalt of this operation is not limited to these. In a general formula (4), as for a compound in case n is 0, the following carboxylic acids (1-10) are mentioned.

[0046]

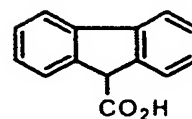
[Formula 8]



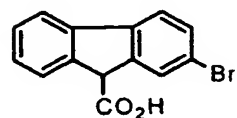
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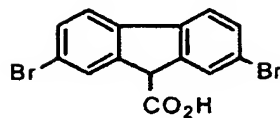
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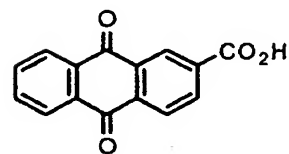
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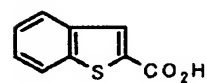
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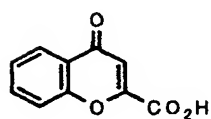
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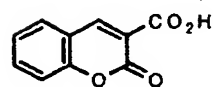
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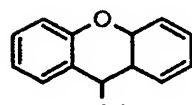
7



8



9



CO₂H

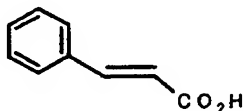
10

[0047]

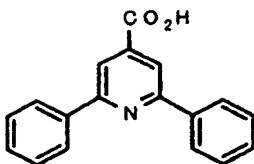
Next, in a general formula (4), n is 1, and, as for a compound in case X is R6 (general formula (5)), the following carboxylic acids (11-15) are mentioned.

[0048]

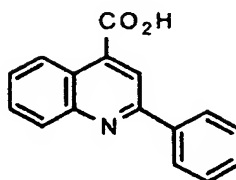
[Formula 9]



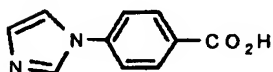
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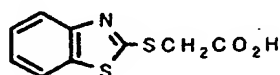
12



13



14



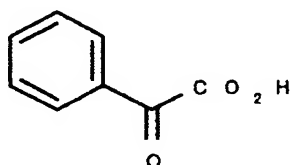
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[0049]

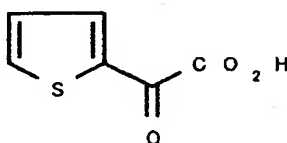
Next, in a general formula (6), as for a compound in case m is 0, the following carboxylic acids (16 and 17) are mentioned.

[0050]

[Formula 10]



16



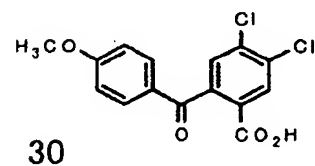
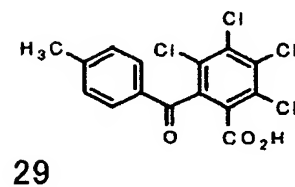
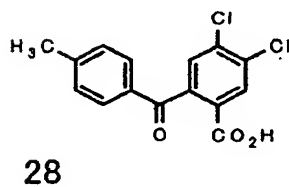
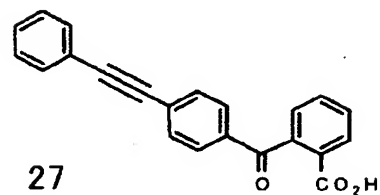
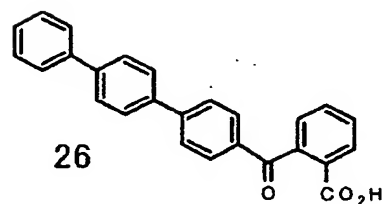
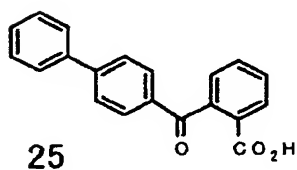
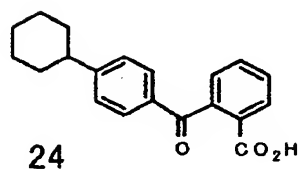
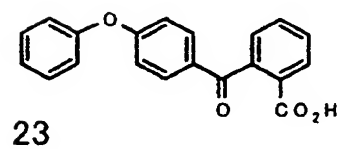
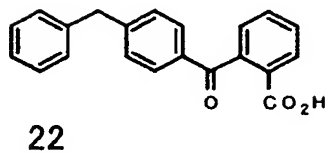
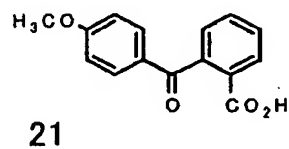
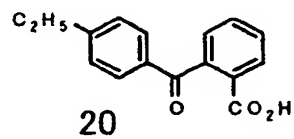
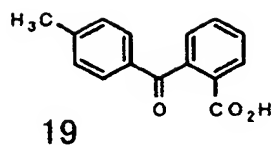
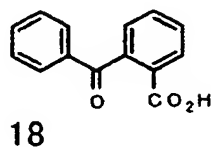
17

[0051]

In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenyl group and R6 is a phenyl group, the following carboxylic acids (18-30) are mentioned.

[0052]

[Formula 11]

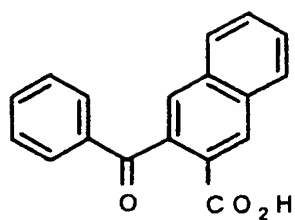


[0053]

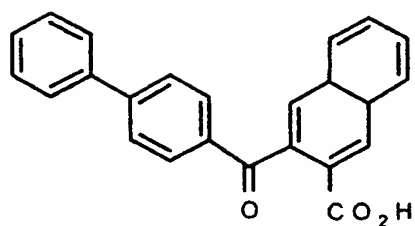
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenyl group and R6 is a naphthyl group, the following carboxylic acids (31-34) are mentioned.

[0054]

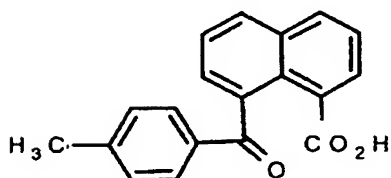
[Formula 12]



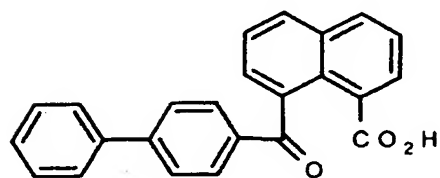
31



32



33



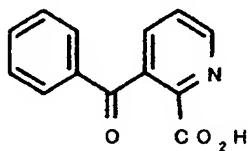
34

[0055]

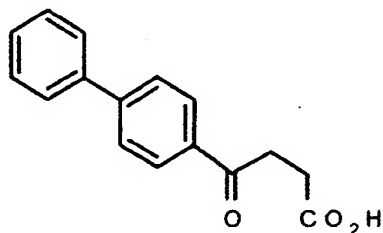
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenyl group and R6 is other radicals, the following carboxylic acids (35-37) are mentioned.

[0056]

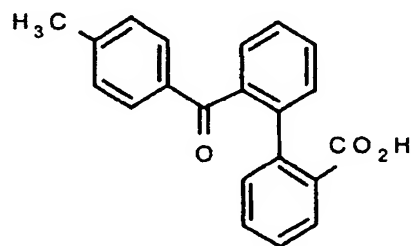
[Formula 13]



35



36



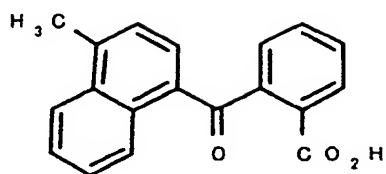
37

[0057]

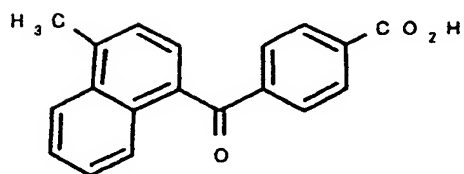
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a naphthyl group and R6 is an aromatic series ring, the following carboxylic acids (38-41) are mentioned.

[0058]

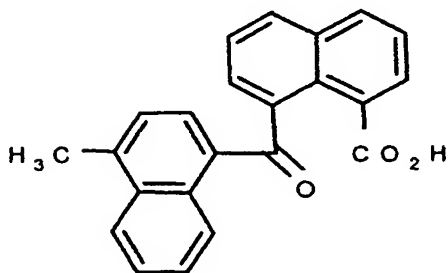
[Formula 14]



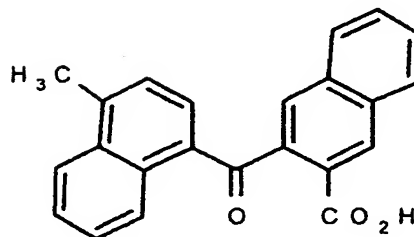
38



39



40



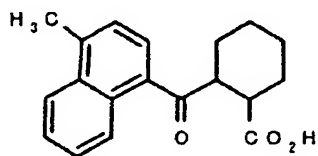
41

[0059]

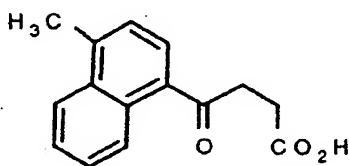
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a naphthyl group and R6 is other radicals, the following carboxylic acids (42-44) are mentioned.

[0060]

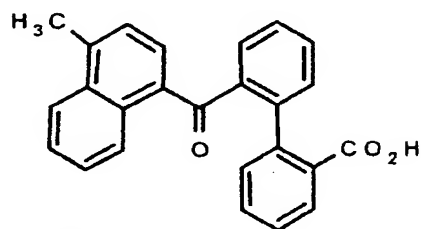
[Formula 15]



42



43



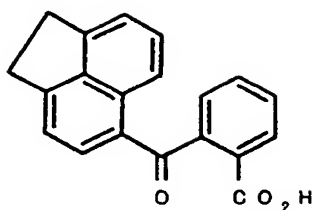
44

[0061]

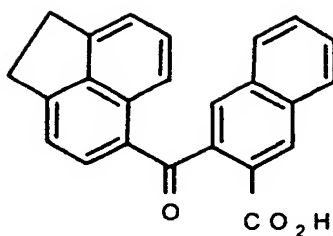
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is an acenaphthyl radical and R6 is a phenyl group and others, the following carboxylic acids (45-48) are mentioned.

[0062]

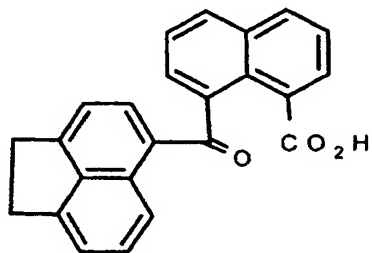
[Formula 16]



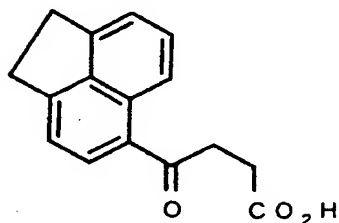
45



46



47



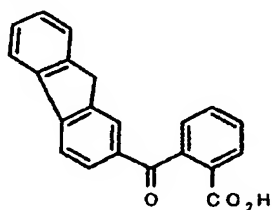
48

[0063]

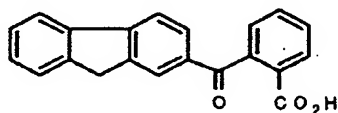
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a fluorenyl group and R6 is a phenyl group, the following carboxylic acids (49-55) are mentioned.

[0064]

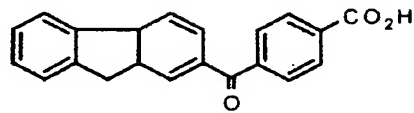
[Formula 17]



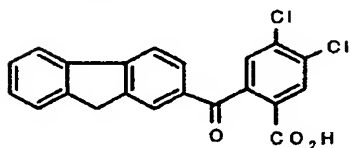
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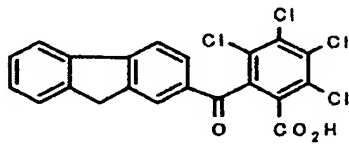
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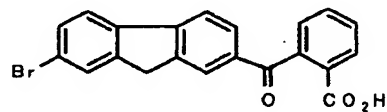
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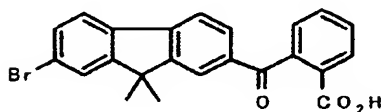
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53



54



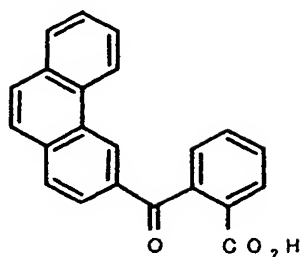
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[0065]

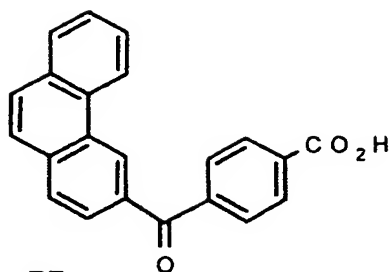
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a phenan TORENIRU radical and R6 is a phenyl group and others, the following carboxylic acids (56-59) are mentioned.

[0066]

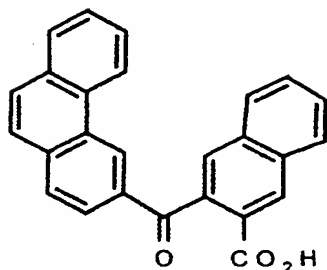
[Formula 18]



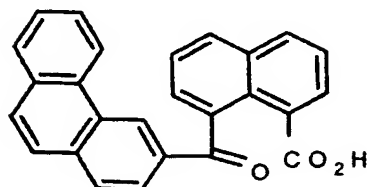
56



57



58



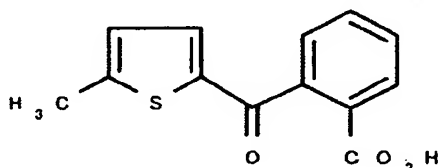
59

[0067]

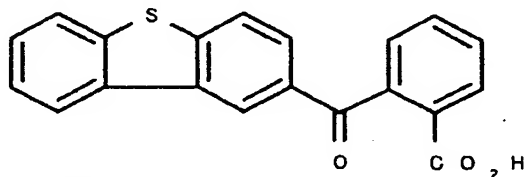
In a general formula (6), it is the case where m is 1 and, as for a compound in case R4 is a heterocycle radical and R6 is a phenyl group, the following carboxylic acids (60 and 61) are mentioned.

[0068]

[Formula 19]



60



61

[0069]

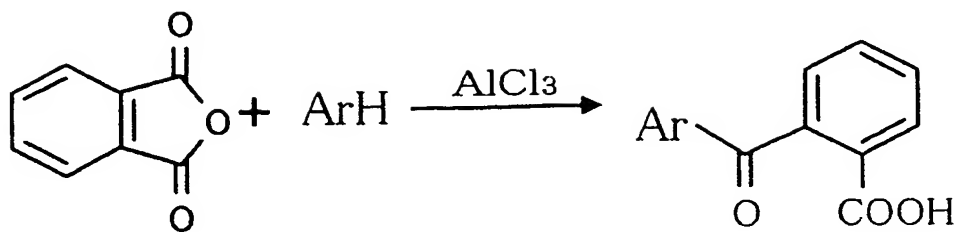
The carboxylic acid with which the carboxylic-acid ion as a ligand in a general formula (4) is guided is compoundable by the well-known synthetic approach. The synthesis method is indicated by the volume composition of an organic compound, 14th volume "reaction (II)" 921st page (1977) Chemical Society of Japan editing of a new experimental science lecture, or for 22nd volume "organic synthesis IV" 1st page (1992) Chemical Society of Japan of the 4th edition experimental science lecture etc., for example. As a typical synthesis method, oxidation reaction of a corresponding primary alcohol and a corresponding aldehyde, the hydrolysis reaction of ester or nitril, the Friedel Crafts reaction by the acid anhydride, etc. are mentioned.

[0070]

Especially, in the Friedel Crafts reaction using the cyclic anhydride of dicarboxylic acid, such as phthalic anhydride, naphthalic acid anhydride, anhydrous amber acid, diphenic acid anhydride, 1, 2-cyclohexane dicarboxylic acid anhydride, 2, and 3-pyridazine dicarboxylic acid anhydride, the carboxylic acid which has a carbonyl group in intramolecular is compoundable. For example, according to the Friedel Crafts reaction using aromatic hydrocarbon or an aromatic heterocycle, and phthalic anhydride, as shown in the following reaction formula, the carboxylic acid which the carbonyl group combined with the ortho position of the benzene ring can compound easily. The carboxylic acid which the carbonyl group combined with the ortho position of the benzene ring is desirable from a complex with high brightness being easy to be obtained compared with a para-position substitution product. In addition, Ar expresses aromatic hydrocarbon or an aromatic heterocycle among a formula.

[0071]

[Formula 20]



[0072]

The same compound as the auxiliary ligand (R2) which consists of a Lewis base in the general formula (2) mentioned above as an auxiliary ligand (R5) which consists of a Lewis base in a general formula (4) is mentioned.

[0073]

a fluorescent substance layer 12 accept for example, an europium complex and a need, and prepare other rare earth ion complexes, other organic fluorescent substances, and an inorganic fluorescent substance as a resin constituent which be made to dissolved or distribute in suitable binder resin, and be mixed, and this be arrange by the approach of spreading and others in the luminescence equipment 10 with which the gestalt of this operation be apply in the location which absorb the light from semi-conductor light emitting devices 11, such as a wall of an external cap 13. As binder resin; thermoplastics, thermosetting resin, a photo-setting resin, etc. are usually mentioned. Specifically, cellulose type resin; epoxy resin; phenol resin; silicone resin, such as styrene resin; polycarbonate resin; polyester resin; phenoxy resin; butyral resin; polyvinyl alcohol; ethyl cellulose, such as methacryl-resin; polystyrene, such as Pori methacrylic acid methyl, and a styrene acrylonitrile copolymer, cellulose acetate, and cellulose acetate butylate, etc. is mentioned.

[0074]

The luminescence equipment 10 with which the gestalt of this operation is applied can emit light in the white light by having with a blue fluorescent substance and a green fluorescent substance, and combining these further, with the red fluorescent substance containing rare earth ion complexes, such as an europium complex. In addition, the fluorescent substance containing other organic red fluorescent substances and an inorganic red fluorescent substance may also be included if needed. A well-known fluorescent substance can be used as a blue fluorescent substance or a green fluorescent substance. For example, as a blue fluorescent substance, inorganic fluorescent substances, such as ZnS:Ag, Sr5(PO4)3Cl:Eu, and BaMgAl10O17:Eu, are mentioned. moreover — as a green fluorescent substance — ZnS:Cu, ZnS:CuAl, and BaMgAl10O17: — inorganic fluorescent substances, such as Eu and Mn, are mentioned. Moreover, in addition to this, a thulium complex is mentioned as a blue fluorescent substance, and organic fluorescent substances, such as a terbium complex, are mentioned as a green fluorescent substance. The carboxylic-acid ion containing beta-diketone anion used for everything but a well-known ligand as a ligand of the europium complex in the gestalt of this operation as a ligand of these complexes or an aromatic series radical can be used.

[0075]

What is necessary is just to arrange the approach of applying the fluorescent substance resin layer containing the mixture of a red fluorescent substance, a blue fluorescent substance, and a green fluorescent substance inside the external cap 13, and forming the fluorescent substance layer 12, or this fluorescent substance resin layer on the semi-conductor light emitting device 11, in order to make the white light emit light. In this case, a red fluorescent substance does not necessarily need to be mixed with a blue fluorescent substance and a green fluorescent substance in the same resin, and the laminating of the resin layer which contains a red fluorescent substance on the resin layer containing a blue fluorescent substance and a green fluorescent substance may be carried out.

[0076]

Next, the gestalt of other operations of the luminescence equipment with which this invention is applied is explained. Drawing 2 is drawing for explaining the luminescence equipment in the gestalt of the 2nd operation. Here, the laminating of the resin layer containing an inorganic fluorescent substance and the fluorescent substance layer containing a complex is carried out one by one on the semi-conductor light emitting device. The external cap 23 the luminescence equipment 20 shown in drawing 2 was formed with a bonnet, glass, etc. in the upper part of a blanket 28 and a blanket 28, Mounting lead 26b and inner lead 26a which were attached in the blanket 28, Mounting lead 26b and inner lead 26a, and flowing electric contact 29. The semi-conductor light emitting device 21 contained in the cup of the mounting lead 26b upper part, The inorganic fluorescent substance layer 27 with which it filled up in the cup of the mounting lead 26b upper part, A rare earth ion complex etc. has the fluorescent substance layer 22 by which mixed distribution was carried out into binder resin, and conductive wire 25a and conductive wire 25b, and, as for the interior of the external cap 23, it fills up with inert gas 24, such as a vacuum or nitrogen gas, and argon gas.

[0077]

In addition, the endurance of a fluorescence complex can be further raised by easing the effect of the heat generated when a semi-conductor light emitting device emits light. For example, the approach of preparing a semi-conductor light emitting device and the fluorescent substance layer which contains a fluorescence complex for space through other layers, such as a partition or a thermal break, and an optical diffusion layer, the approach of carrying out the laminating of a heat-resistant inorganic high fluorescent substance layer and the fluorescent substance layer containing a fluorescence complex, etc. are mentioned. The heat deterioration of the fluorescent substance containing the complex which consists of an organic material which is generally inferior to thermal resistance by this compared with an inorganic fluorescent substance can be suppressed, and luminescence equipment excellent in endurance can be obtained.

[0078]

For example, it is desirable that the layer which consists of an inorganic fluorescent substance, and the layer of the fluorescent substance containing a complex are the layered products separated, respectively when a fluorescent substance approaches the semi-conductor light emitting device 21 and is arranged like the luminescence equipment 20 shown in drawing 2, and it is desirable that it is the layer of the direction with the inorganic fluorescent substance

layer near a light emitting device. That is, the heat generated by luminescence of the semi-conductor light emitting device 21 can ease heating the fluorescent substance layer 22 locally by arranging the inorganic fluorescent substance layer 27 which contains an inorganic fluorescent substance between the semi-conductor light emitting device 21 and the fluorescent substance layer 22 containing a complex. Moreover, in the case of the shell mold configuration which is the general gestalt of LED, a fluorescent substance is also mixable in closure resin, such as an epoxy resin. In this case, the light from a fluorescent substance turns into light diffused more.

[0079]

The luminescence equipment 10 and the luminescence equipment 20 with which the gestalt of this operation is applied are independent, or can be used as various lighting systems by combining plurality. As a lighting system, a lighting lamp, the back light for liquid crystal panels, super-thin lighting, etc. are mentioned, for example.

[0080]

[Translation done.]

* NOTICES *

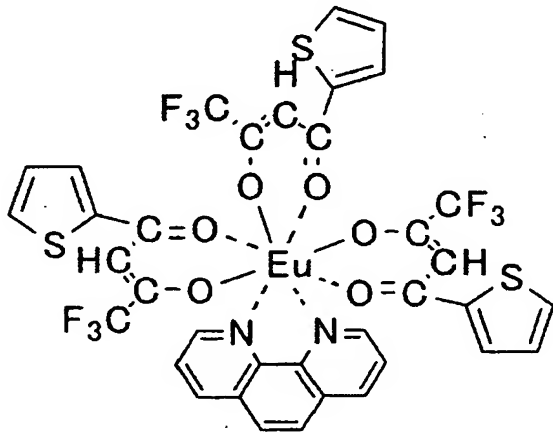
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EXAMPLE

[Example]
An example is given to below and the gestalt of this operation is explained more concretely. In addition, the gestalt of this operation is not limited to an example. Moreover, the section in an example and especially % are weight criteria altogether, unless it refuses.
(Examples 1-2, example of a comparison)
The europium (Eu) complex 10 section which makes a ligand beta-diketone shown by the following formula, and the methyl-ethyl-ketone solution (20% of concentration) 200 section of a polyvinyl butyral (Sekisui Chemical Co., Ltd. make S lek BL-1) were mixed, and the mixed solution was prepared, and these mixed solutions 0.2-0.3g were applied to the interior of glass ampul with a diameter of 14mm, it dried, and the coat of a fluorescent substance was formed. Next, this ampul was processed on the conditions ((1) vacuum lock (2.5x10 to 5 torrs), (2) nitrogen gas charging (20 ppm or less of oxygen densities), (3) air enclosure (about 20% of oxygen densities)) shown in a table 1, and the coat of the fluorescent substance containing Eu complex created the glass ampul applied to the inner surface. Next, the light from ultraviolet to a visible region was irradiated in this glass ampul for 40 hours using the fading-test machine (Ci4000 by the atlas company), respectively, and the fluorescence intensity of the fluorescent substance containing an europium (Eu) complex was measured after that using the Hitachi fluorescence spectrometry machine F4500. The fluorescence intensity of a fluorescent substance is expressed as a characteristic which set fluorescence intensity when not irradiating light by the fading-test machine to 100. Lightfastness is so good that a numeric value is close to 100. A result is shown in a table 1.

[0081]
[Formula 21]



[0082]
[A table 1]

	実 施 例		比較例
	1	2	
	真空	窒素ガス	空気
光照射時間 0	1 0 0	1 0 0	1 0 0
4 0 時間	9 0	8 2	0 . 3

[0083]

When irradiating light from the result of a table 1 at the fluorescent substance put on the vacua (example 1), and when irradiating light at the fluorescent substance put on the bottom of nitrogen-gas-atmosphere mind (example 2), the lightfastness of a fluorescent substance is good and each is understood that endurance improves. On the other hand, when light is irradiated at the fluorescent substance placed into air (example of a comparison), it falls to 30% 40 hours after, and it turns out that lightfastness is remarkably poor.

[0084]

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing for explaining the luminescence equipment with which the gestalt of this operation is applied.

[Drawing 2] It is drawing for explaining the luminescence equipment of the gestalt of the 2nd operation.

[Description of Notations]

10 20 [— 14 An external cap, 24 / — Inert gas, 15a, 15b 25a, 25b / — A conductive wire, 16a, 26a / — An inner lead, 16b, 26b / — 18 A mounting lead, 28 / — 19 A blanket, 29 / — Electric contact, 27 / — Inorganic fluorescent substance layer] — 11 Luminescence equipment, 21 — 12 A semi-conductor light emitting device, 22 — 13 A fluorescent substance layer, 23

[Translation done.]

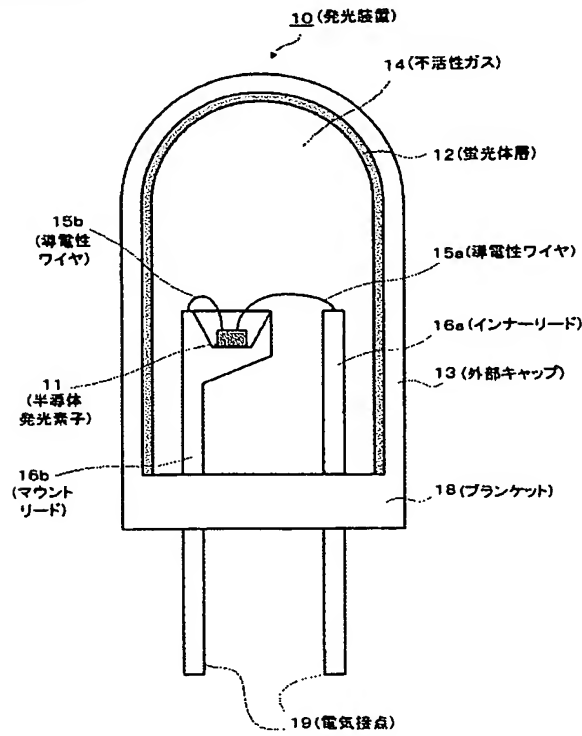
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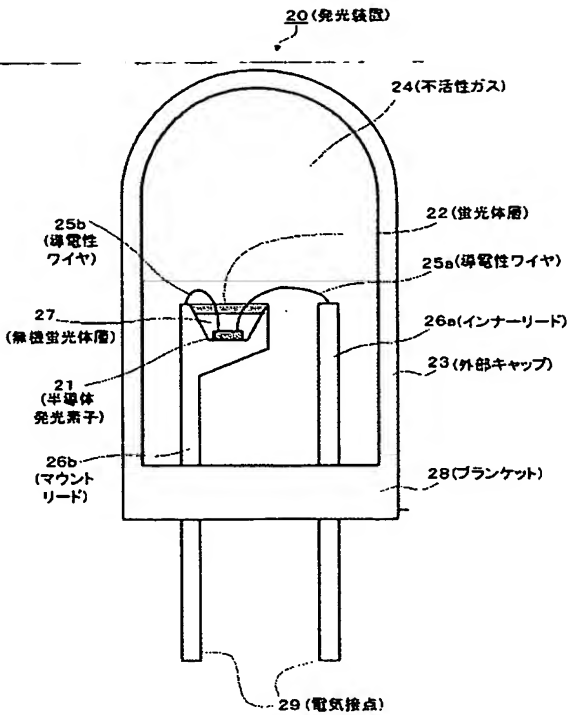
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DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]